INTERLABORATORY
STUDY 93-2
JULY 1993

ORGANOCHLORINE PESTICIDES (OC's)

IN SUPPORT OF

THE INTEGRATED
ATMOSPHERIC
DEPOSITION
NETWORK
(IADN)

JUNE 1994

Ontario

Environment Canada
Environnement Canada

Atmospheric Environment Service
Service de l'environnement atmosphérique

ISBN 0-7778-2794-8

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Report Prepared by

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for

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Laboratory Services Branch
Ontario Ministry of Environment and Energy
PIBS No. 3101

and

Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
ARD Report No. 94-006

The author gratefully acknowledges and thanks George Steinke and Sathi Selliah for the preparation of materials, and Don King, Renata Baily, Syed Iqbal, and Maris Lusis for their help in reviewing the results.

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1 SUMMARY OF INTERLABORATORY STUDY 93-2

Interlaboratory Study 93-2 was the second study for Organochlorine Pesticide (OC) analysis initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an assessment of laboratory variability. Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards. A seventh laboratory withdrew from the study. Two ampoules (OC1 and OC2) were for direct instrumental analysis and two (OC3 and OC4) required analytical Clean-up before instrumental analysis. The parameter list consisted of 18 different OC's. All 18 compounds were present in each ampoule.

The interlaboratory mean and median for the Injection-Ready solutions demonstrated good agreement with the target values (< 15% difference). Overall agreement with the target has improved from 50-60% of the results being in the range 90-110% of the target in the first study[4], to 70-80% of the results in this study being in the range 90-110% of target. Between-laboratory variability at the higher concentration level is similar to the first study[4] among these participants, though many parameters have improved from ±20% to ±10-15%. Between-laboratory variability at the lower concentration is more variable in this study than the previous study[4], suggesting that several participants have intercept problems.

The interlaboratory mean and median for the solutions processed through Clean-up also demonstrated good agreement with the target (< 15% difference), except for Heptachlor Epoxide, Methoxychlor and Endosulfan I in OC3 and Methoxychlor in OC4 (differ by 15-35%). There was no statistically significant difference between the means or variances of the injection solution vs. the Clean-up solution at the higher concentration level for any of the parameters ($\alpha = 0.05$). However, at the lower concentration, there was a statistically significant difference in the means between the injection solution and the Clean-up solution for two parameters ($\alpha = 0.05$). There were statistically significant differences in the variances between the low concentration injection solution and Clean-up solution for eight parameters ($\alpha = 0.05$). For several parameters in different laboratories, the Clean-up procedure adds and interferant, while for other parameters or laboratories, the Clean-up procedure appears to retain some of the target analytes. This did not appear critical at the higher concentration level but may be critical at the lower concentration level. None of these problems appears to be compound-specific. Individual laboratories need to investigate the possible sources of these biases, such as contamination of the packing material, solvent used, or problems in fractionation.

The participants in this interlaboratory study demonstrate an improvement in performance from the previous interlaboratory study[4]. Individual participants may have a problem with some individual compounds that require individual attention. It is the intent to continue with future interlaboratory studies in support of the IADN program, assessing not only between-laboratory comparability for calibration and Clean-up, but to include spiked matrix samples for precipitation and ambient air to assess between-laboratory method comparability.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was the second in a series designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[2]. This interlaboratory study provides information on the laboratory component of between agency differences, can be used to help establish the comparability of the data sets, and is a recommended activity of the IADN Quality Assurance Program Plan[3]. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination of the study was done by AES and preparation of all materials was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 93-2 targets laboratories analyzing for Organochlorine Pesticides (OC's) in precipitation and/or ambient air. The aim of this study was to continue to monitor the comparability among the participating laboratories. Two aspects of OC analysis were addressed in this study: comparability of instrumental calibration and analytical Clean-up of interferences. Two ampouled standards ready for direct instrumental analysis and containing all 18 OC's on the target list, were provided to assess calibration. Two additional ampoules containing an interferant and therefore requiring Clean-up, were also provided to the participants.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

Neat OC's of 99%+ purity were purchased from Ultra Scientific and Supelco by AES. All subsequent work was done by the QMU of LSB, MOEE. Three concentrated stock solutions containing six compounds each were prepared in 2% toluene/iso-octane, and sealed into 5 mL amber ampoules. The stock concentrations were between 10 to 15 mg/L and verified using gas chromatography/electron capture detector (GC/ECD) analysis by an analytical

unit at LSB not involved in analysis of ambient air or precipitation. Ampouled solutions were stored in a freezer at -20°C.

Solutions for this interlaboratory study were prepared from the concentrated stock solutions by diluting appropriate aliquots into a combined solution in iso-octane. Concentrations were chosen to fall within the routine instrumental calibration range of the participants. The first two solutions were sealed in 5 mL amber ampoules and labelled 93-2-OC1 and 93-2-OC2. The second two solutions were prepared at the same concentration as the first two, with the addition of an aliquot of vegetable oil at the same concentration range as the OC's. These solutions were also sealed in 5 mL amber ampoules and labelled 93-2-OC3 and 93-2-OC4. (Further reference to these ampoules eliminates "93-2-".) All ampoules were stored in a freezer at -20°C until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on July 27, 1993. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the solutions by their routine in-house methods used to analyze ambient air or precipitation samples for the IADN program. Two solutions (OC1 and OC2) were ready for direct instrumental injection and participants were asked not to do any sample preparation steps. Participants were specifically asked to process ampoules OC3 and OC4 through their routine analytical Clean-up procedure prior to instrumental analysis. Participants were requested on the report form provided (Appendix 2) to summarize their Instrument, Detector and GC column used for the analysis, as well as Clean-up conditions. All participants were assigned a unique identification code that does not correspond to the order the participants are listed in Appendix 2.

3.4 Data Reporting

Results were submitted to AES in written form. All data were manually entered by laboratory code into an electronic spreadsheet. One laboratory withdrew from the study due to a lack of appropriate standards and their name was withdrawn from the list of participants.

The participating laboratories were mailed a copy of the tables of results on November 19, 1993. One participant noted a transcription error for 6 values in from one of the duplicate sets of results they submitted for ampoule OC3 (duplicate results were originally provided and the same values were entered into the spreadsheet for both the "A" and "B" set of results). The correct values were entered into Table 3 for the "B" set of results for OC3. One other participant submitted revisions of the decimal place values to one set of their results (they originally provided multiple sets of results using different analytical procedures). For this participant, both sets of results are included in the tables, with the original values in parentheses. Their comments are discussed in the

individual laboratory review. A revised Table of results was sent to the participants on December 8, 1993.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each parameter in each of the ampoules for which there were 2 or more results reported, and are included in Tables 1-4, Appendix 1. As the data set is small, these calculated values are provided as an approximate indicator of the spread of the data, and may not necessarily be statistically correct. For p,p-DDD in Ampoules OC1 and OC2, Laboratory 9326's results were excluded from the calculation of the interlaboratory mean, median, SD and %RSD. The explanation for this is given in the individual review of this participant's results in Section 4.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

Results were received from all of the participants who received the ampouled solutions. Qualifying remarks from the participants are provided in the individual laboratory review below.

For all parameters in the Injection-Ready solutions, the interlaboratory mean and median demonstrate good (< 15% difference) agreement with the target (Tables 1 and 2), excluding o,p-DDE, which was on the target list of only one participant. The mean and median of most parameters in the solutions processed through Clean-up (OC3 and OC4) also differed from the target by < 15% except for Heptachlor Epoxide, Methoxychlor and Endosulfan II in OC3, and Methoxychlor in OC4 (Tables 3 and 4). Agreement among the participants is good at the higher concentration level (OC2 and OC4, Tables 2 and 4), with the %RSD being in the range of 7-22%, except for Methoxychlor in OC2 (Table 2). The level of between-laboratory variability for the high concentration Injection-Ready Ampoule (OC2) is similar to the same concentration levels observed in the first study among this group of participants[4], though there is some improvement from ± 15-20% to ± 10-15% in this study.

Between-laboratory relative variability is greater at the lower concentration level (OC1 and OC3, Tables 1 and 3), with the %RSD as high as 30-46% for several parameters. This is expected behaviour of analytical systems at lower concentrations (see Appendix 3 of Ref. 4). The level of between-laboratory variability for several parameters in the low concentration Injection-Ready Ampoule (OC1) is greater than the same concentration levels observed in the first study among this group of participants[4]. The higher level of variability at the lower concentration level for these parameters suggests that some participants may have either an intercept problem or some degree of non-linearity.

The overall agreement with the target has improved in this study compared to the first study (Interlaboratory Study 92-3[4]) among this group of participants. In Study 92-3 approximately 50-60% of the participants' results were in the range 90-110% of the target. In this study, approximately 70-80% of the participants' results are in the range 90-110% of the target for the Injection-Ready ampoules (Table 6 and Figure 35).

There is greater spread in the results when the ampoules were processed through Clean-up (Table 7 and Figure 36). Only 23-60% of the participants' results were in the range 90-110% of the target. Possible causes for this are discussed in detail below.

To aid in evaluating the results, a graphical technique was used for all parameters except o,p-DDE (only one participant reported results for this parameter). As each parameter had a "pair" of results, either Ampoule OC1 and OC2 (Injection-Ready Ampoules), or OC3 and OC4 (Ampoules for Clean-up), these results may be plotted on an X-Y plot using the Youden technique[5]. The result from Ampoule 1 or 3 is plotted on the vertical axis and the corresponding result from Ampoule 2 or 4 is plotted on the horizontal axis. The interlaboratory mean for each ampoule is also plotted.

The graphs are divided into four quadrants, with the intersection point at the target values. The data points should cluster around the target if random error is the only source of variability. Results in the upper right quadrant are considered biased high and those in the lower left quadrant are biased low. The main source of this type of variability is a difference in analytical standards or inadequate calibration practices. Data points that fall in the lower right or upper left quadrants are considered erratic or out-of-control. Sources of this type of error are more difficult to ascertain. Sources of erratic performance for the Injection-Ready Ampoules could be poor sample injection into the gas chromatograph, a septum leak, poor chromatography if contamination remained from a previous sample, or other instrumental problems. These potential sources of error may be compounded in the Ampoules for Clean-up by air pockets in the Clean-up column, contaminated packing material in the Clean-up column, poor solvent flow, errors in fractionation or losses during the final evaporation step.

Within-laboratory precision may be assessed by drawing a line between the origin and the intersection of the target values. The closer the data point is to this diagonal line, the better the within-laboratory precision.

The results from Ampoules OC1 and OC2 for α-Hexachlorocyclohexane (α-HCH) show good agreement with the target for all participants (Figure 1). The Clean-up procedure introduces greater variability in the results (Figure 2). There was a statistically significant difference in the variances of OC1 and OC3 ($\alpha = 0.05$), but not for the variance of OC2 and OC4. Laboratories 9325B and 9326 were erratic for OC3 and OC4.

Similar results are observed for γ-HCH in Ampoules OC1 and OC2 (Figure 3) as for α-HCH. The Clean-up again introduces greater variability among the participants (Figure 4), though Laboratory 9326 does not differ from the γ-HCH target as much as from the α-HCH target. There was a statistically significant difference in the variances of OC1 and OC3 ($\alpha = 0.05$), but not for the variances of OC2 and OC4. Laboratory 9325B reported a high result for OC3 and is erratic (Figure 4).

The results for p,p-DDT demonstrate spread along the diagonal line (Figure 5), suggesting differences among the participants' calibration standards. Excluding Laboratory 9325B, there appears better agreement among the participants for the ampoules processed through Clean-up (Figure 6). However the Clean-up appears to have added an interferant that affects the quantitation of p,p-DDT for several participants. Except for Laboratories 9323A and 9327, the other participants have reported larger differences from the target in OC3 and OC4 (Clean-up), compared respectively to differences form the target of OC1 and OC2 (no Clean-up). Laboratories should confirm that the column packing material is properly pretreated prior to use in the Clean-up stage, to avoid possible contamination.

Similar results were observed for o,p-DDT in Ampoules OC1 and OC2 (Figure 7) as for p,p-DDT. A greater spread in results was observed when the ampoules were processed through the Clean-up (Figure 8). Laboratory 9325A appears to lose o,p-DDT

during Clean-up, as they are biased low for OC3 and OC4 but had very good agreement with the target for OC1 and OC2. There was a statistically significant difference in the variances of OC1 and OC3 ($\alpha=0.05$), but not for the variances of OC2 and OC4. Laboratory 9325B is again erratic for the ampoules processed through Clean-up.

The results for p,p-DDD demonstrate the same pattern (Figure 9) as the results for α-HCH and γ-HCH. There is a slight positive increase in the results for the ampoules (OC3 and OC4) processed through Clean-up (Figure 10). The difference in the means for OC2 and OC4 is not statistically significant ($\alpha=0.05$), but the difference in the means for OC1 and OC3 ($\alpha=0.05$) is significant. This suggests that the Clean-up process may be adding material that interferes with the quantitation of p,p-DDD. This does not appear critical at higher concentrations but may be at lower concentrations. Further investigation is necessary to determine possible sources of this bias.

Only three participants have o,p-DDD on their target list. Closer agreement among the participants is demonstrated by the ampoules processed through Clean-up (Figure 12) than the Injection-Ready ampoules (Figure 11). However there is no statistically significant difference in the means or variances ($\alpha=0.05$), for OC1 and OC3 or OC2 and OC4. Laboratory 9324 appears slightly erratic for OC1 and OC2 (Figure 11).

The distribution of p,p-DDE results from the Injection-Ready ampoules (Figure 13) demonstrate a normally random pattern expected from a Youden plot[5]. Laboratory 9324 is somewhat erratic. The results from the ampoules processed through Clean-up demonstrate better within-laboratory precision (Figure 14), as most of the results fall on the diagonal line. Laboratory 9325B is again erratic for the ampoules processed through Clean-up.

The results for α-Chlordane demonstrate good agreement with the target and among the participants (Figure 15), except for Laboratory 9326 who is biased high. The high values from Laboratory 9326 shifts the interlaboratory mean away from the other participants and the target value. If Laboratory 9326's results are excluded, the interlaboratory mean for OC1 is 4.66 and for OC2 is 22.85. These values are more representative of the other participants' results and are much closer to the target. The same good agreement is demonstrated with the ampoules process through Clean-up (Figure 16), including Laboratory 9326. Possible reasons for Laboratory 9326's performance are discussed in the individual review below. However Laboratory 9325B is again biased high and erratic for the ampoules processed through Clean-up.

Good agreement with the target and among the participants is demonstrated for γ-Chlordane (Figure 17). Laboratory 9322 is biased slightly high for OC2. The performance remains consistent for the ampoules processed through Clean-up (Figure 18), except for Laboratory 9325B, who is again erratic. There was a statistically significant difference in the variances of OC1 and OC3 ($\alpha=0.05$), but not for the variances of OC2 and OC4.

There is a slight high bias among all of the participants for Heptachlor Epoxide at the lower concentrations (OC1, Table 1 and OC3, Table 3), suggesting a possible intercept problem. A normal distribution around the target is demonstrated for OC2 and OC4 (Tables 2 and 4). There is a typically random Youden plot demonstrated by the Injection-Ready ampoules (Figure 19), though with a positive shift along the Y-axis. The overall performance appears the same for the ampoules processed through Clean-up (Figure 20), except for Laboratory 9325B, who is again erratic. The result from Laboratory 9325B for OC3 appears to noticeably shift the mean, as there is a

statistically significant difference between the means of OC1 and OC3 ($\alpha = 0.05$), though there is no significant difference in the variances ($\alpha = 0.05$). There is no statistically significant difference in the means or variances of OC2 and OC4 ($\alpha = 0.05$).

The results for Methoxychlor in the Injection-Ready ampoules (Figure 21) demonstrate biases among the participants that are typically attributed to a difference in standards. Except for Laboratory 9325C, the Clean-up process appears to "add something", as the Methoxychlor results are all shifted high along the Y-axis (Figure 22). Laboratories should confirm that the column packing material is properly pretreated prior to use in the Clean-up stage, to avoid possible contamination. There was a statistically significant difference in the variances of OC1 and OC3 ($\alpha = 0.05$), but not for the variances of OC2 and OC4. The ND of Laboratory 9325C in OC3 (shown in Figure 22) is the most likely cause for this difference in variability between OC1 and OC3. Laboratory 9325B demonstrated erratic behaviour for the Clean-up samples (Figure 22).

Most of the participants agreed with the target for Dieldrin in the Injection-Ready ampoules (Figure 23), though Laboratory 9323A was biased high. Laboratory 9325B had problems detecting Dieldrin in OC1, resulting in erratic performance. The same grouping was demonstrated for the ampoules processed through Clean-up (Figure 24). However Laboratory 9325B had problems with the lower concentration ampoules (OC1 and OC3). This is discussed further in the individual laboratory review.

Greater spread in Hexachlorobenzene (HCB) results is observed among the participants at the higher concentration (OC2 - %RSD = 17.3%) than the lower concentration (OC1 - %RSD = 9.8%) in Figure 25. This suggests some slope problems among some of the participants. The Clean-up process increases the spread among the participants (Figure 26), more noticeably at the lower concentration level, as Laboratory 9325B is again erratic. There was a statistically significant difference in the variances of OC1 and OC3 ($\alpha = 0.05$), but not for the variances of OC2 and OC4.

Only four participants reported results for Endrin. Agreement among the participants and to the target has improved noticeably compared to the first study among these participants[4]. In this study the %RSD ranges from 3.7 to 15.4%, while in the previous study the %RSD ranged from 26.8 to 33.03%. There is a slight high bias at the lower concentration level (Figure 27). Performance is similar for the ampoules processed through Clean-up (Figure 28), though Laboratory 9324 is biased slightly low.

Most participants agreed with the targets for Endosulfan I in the Injection-Ready ampoules (Figure 29), except for Laboratory 9322 who was biased high, and Laboratory 9325B who had problems detecting Endosulfan I in OC1. Laboratory 9325B improved its performance for OC3, and reported results that agreed with the target and the majority of other participants (Figure 30), though Laboratory 9322 was biased high. This resulted in a considerable reduction in the value for the Standard Deviation at the lower concentration level (OC1 and OC3). There was a statistically significant difference in the variances between OC1 and OC3 ($\alpha = 0.05$), but not for the variances of OC2 and OC4. Laboratory 9325C's Clean-up procedure appears to add an interferant, as their results for OC3 and OC4 are biased slightly high compared to their results for OC1 and OC2.

Most of the participants agreed with the target for Endosulfan II in the Injection-Ready ampoules (Figure 31), though Laboratory 9323A was biased high. The same grouping was demonstrated for the ampoules processed through Clean-up (Figure 32), except for Laboratory 9325B, which had problems with the lower concentration ampoules

(OC1 and OC3) and was erratic. This is discussed further in the individual laboratory review. There was a statistically significant difference in the variances between OC1 and OC3 ($\alpha = 0.05$), but not for the variances of OC2 and OC4.

The results for Oxychlordane in OC1 with no Clean-up (Figure 33) show greater spread than OC3 with Clean-up (Figure 34). However there is no statistically significant differences in the variances ($\alpha = 0.05$). Performance is consistent at the higher concentrations (OC2 and OC4), though there is a slight negative bias of the interlaboratory means, suggesting that some participants may have a slope problem. Laboratory 9325B demonstrated erratic behaviour for OC1 and OC3 (Figures 33 and 34).

The between-laboratory performance at the higher concentration level does not appear to change noticeably between the instrumental analysis only (OC2) and when the Clean-up procedure is included (OC4). For none of the parameters was there a statistically significant difference between the interlaboratory means and variances of OC2 and OC4 ($\alpha = 0.05$). However at the lower concentration level (OC1 and OC3), there were statistically significant differences in the interlaboratory means for p,p-DDD and Heptachlor Epoxide. There were statistically significant differences in the variances of OC1 and OC3 for α-HCH, γ-HCH, o,p-DDT, γ-Chlordane, Methoxychlor, HCB, Endosulfan I, and Endosulfan II ($\alpha = 0.05$). Except for o,p-DDT and Methoxychlor, the differences in the mean and variances for the other listed parameters can be attributed to the problems Laboratory 9325B had with their analysis at the lower concentration level. This is discussed in detail below. For o,p-DDT, Laboratories 9325A and 9325B had problems with the analysis of OC3 (Table 3 and Figure 8). For Methoxychlor, Laboratory 9325C had problems with the analysis of OC3 (Table 3 and Figure 22). This suggests that the Clean-up process may be adding an interferant or retaining the compound, that impedes the quantitation of several parameters in the above mentioned instances. As noted, this does not appear critical at higher concentrations but may be at lower concentrations. Ensuring that the materials used for the Clean-up process are free of interferants is important to prevent this type of problem. Further investigations are necessary to determine other possible sources of this type of problem.

INDIVIDUAL LABORATORY PERFORMANCE

While most of the participants in this study are the same laboratories that participated in Interlaboratory Study 92-3[4], the laboratories have been assigned different ID Codes in this study. Therefore the following individual laboratory review is based only on the results of this study, with no comparisons to previous studies, so as to maintain laboratory confidentiality.

Laboratory 9322

Laboratory 9322 was biased high relative to the target and to the other participants for most of their results (Table 6 and Figures 35 and 36). Within-laboratory precision was good for p,p-DDT (Figures 5 & 6), o,p-DDT (Figures 7 & 8), and Methoxychlor (Figure 21 & 22). However for the other parameters, Laboratory 9322 tended to be biased high for OC2 and OC4, with their data point frequently falling along the horizontal target line of OC1 and OC3, but to the right of the vertical target line of OC2 and OC4. Prominent examples are α-HCH (Figure 1 & 2), α-Chlordane (Figure 15 & 16), and Endosulfan II (Figures 31 & 32). This suggests that Laboratory 9322 has a positive slope bias for several parameters. Comparison of their calibration standards

along the full calibration range with corresponding standard reference materials should help correct the high bias and the slope problem.

Their Clean-up procedure may also contribute to their high bias. Approximately 57% of their results were greater than 110% of the target in OC1 and OC2 (Table 6, no Clean-up). However 73% of their results for OC3 and OC4 (Clean-up) were greater than 110% of the target (Table 6). Careful confirmation that the column packing material is properly pretreated prior to use in the Clean-up stage, to avoid possible contamination, as well as checks of other materials used, could help reduce this type of bias.

Laboratory 9323

Laboratory 9323 provided a single set of results for the instrumental injection ampoules (OC1 and OC2), but provided a duplicate set of results for the solutions requiring Clean-up (OC3 and OC4). The duplicate sets of results were labelled "A" and "B". The single set of results for OC1 and OC2 were labelled "9323A". As noted in Section 3.4, the initial table of results for OC3 had transcription errors for six of the parameters. The "A" results had been entered in both columns for Dieldrin, HCB, Endrin, Endosulfan I, Endosulfan II, and Oxychlordane. Laboratory 9323 reported this and the correct "B" results were entered in the updated tables.

Their results for the Injection-Ready solutions (OC1 and OC2) had the majority of their results within 90-120% of the target and the remainder biased high (Table 6 and Figure 35). Dieldrin (Figure 23) and Endosulfan II (Figure 31) appear to be problem parameters and were biased noticeably high. However within-laboratory precision was good, with all their data points being on or close to the diagonal line (Figures 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, and 33).

The Clean-up procedure used by Laboratory 9323 appears to retain some of the parameters. Eight of the "A" and three of the "B" results were in the range 80-90% of the target (Table 6) compared to none of the OC1 and OC2 results being in this range. Five of the "A" and eleven of the "B" results for OC3 and OC4 were greater than 110% of the target compared to 18 of the OC1 and OC2 results (Table 6).

The within-laboratory agreement between the duplicate Clean-up results is better for OC3 than for OC4. Only the results for p,p-DDT and Dieldrin differ by more than 10% but less than 15% in OC3. In OC4, the duplicate Clean-up results differ by less than 10% only for α-HCH, Endosulfan I, and Oxychlordane. All the other results for OC4 differ by more than 10% but less than 20%. However this level of within-laboratory precision is considered good for organic analysis.

Laboratory 9324

Laboratory 9324 had approximately 75% of their results for OC1 and OC2 in the range 80-120% of the target (Table 6 and Figure 35). Except for Methoxychlor, p,p-DDT, p,p-DDD, and Endosulfan II, the majority of their results are in the upper left quadrant of the Youden plots (Figures 1, 3, 7, 11, 13, 15, 17, 19, 23, 25, 27, 29, and 33). However, out of these, only γ-Chlordane differs from the interlaboratory mean by more than 2 Standard Deviations (Tables 1 and 2). The pattern of these results suggest that Laboratory 9324 has a high intercept and negative slope problem, as the results for OC1 (low concentration) are high and the results for OC2 (high concentration) are low. Comparison with standard reference materials across the full calibration range may help solve this problem.

Laboratory 9324 indicated that results for Endosulfan II in the ampoules processed through Clean-up (OC3 and OC4, Tables 3 and 4) were Not Available (N/A), though results had been reported for OC1 and OC2. No explanation was provided.

Laboratory 9324 was the only participant to have o,p-DDE on their target list. They were low relative to the target in OC1 and OC2 (Injection-Ready solutions), but were high relative to the target in OC3 and OC4 (processed through Clean-up). A similar effect is observed for o,p-DDT and HCB, though the values for these parameters in the Injection-Ready solutions (OC1 and OC2) were higher than the target value. These results suggest that their Clean-up procedure adds an interferant to the sample. They should confirm that the column packing material is properly pretreated prior to use in the Clean-up stage, to avoid possible contamination.

At the lower concentration level, Laboratory 9324 had better agreement with the target in the ampoule processed through Clean-up (OC3) than with the direct injection solution (OC1) for p,p-DDT, o,p-DDD, p,p-DDE, α-Chlordane, γ-Chlordane, Heptachlor Epoxide, Methoxychlor, Dieldrin, Endrin, Endosulfan I and Oxychlordane. The results changed by as much as 15-24% for several of these parameters. At the higher concentration level, the results for these parameters were approximately the same (within 10%) between OC2 (no Clean-up) and OC4 (Clean-up). For α- and γ-HCH, agreement with the target was better for OC1 and OC2 (no Clean-up) than for OC3 and OC4 (Clean-up), though the difference was only -5% between OC1 and OC3, and -3% between OC2 and OC4. For all of these parameters, it appears that the Clean-up procedure retains some fraction of these target parameters. This does not appear to be critical at higher concentrations but may be critical at lower concentrations. Program needs of this laboratory may determine how important this problem is and whether investigation into their Clean-up materials is required.

Laboratory 9325A, B & C

Laboratory 9325 initially provided two sets of results, using two different Clean-up procedures for OC3 and OC4, and two different instrumental techniques for all of the ampoules. The results were labelled "A" and "B". Prior to the release of the tables of results to the participants, Laboratory 9325 modified their Clean-up technique to a single-fraction analysis. As extra solutions were available, they repeated their analysis using their revised method and submitted a third set of results. These were labelled "C". Details of the different procedures are provided in Table 5. In the following discussion, each analytical procedure will be discussed separately. An overview follows at the end of the discussion for 9325C.

Laboratory 9325A

Laboratory 9325A had 90% of their results for the injection-ready solutions (OC1 and OC2) within 80-110% of the target (Table 6 and Figure 35). Only for p,p-DDE were they biased low, though they were within 2 Standard Deviations of the mean (Tables 1 and 2). They demonstrated good within-laboratory precision almost all parameters (Figures 1, 3, 5, 7, 9, 13, 15, 17, 19, 21, 23, 25, 29, 31, and 33).

Their results for OC3 and OC4 demonstrated more variability relative to the target (Table 6 and Figure 36). They had problems with the analysis of o,p-DDT in OC3, where they were biased very low (Table 3 and Figure 8). For p,p-DDT, α-chlordane, γ-Chlordane, Heptachlor Epoxide, Dieldrin, Endosulfan I, Endosulfan II, and Oxychlordane, higher values are reported in OC3 and OC4 (Clean-up) as compared to OC1 and OC2 (no Clean-up), respectively. These results suggest that their Clean-up

procedure adds an interferant to the sample. They should confirm that the column packing material is properly pretreated prior to use in the Clean-up stage, to avoid possible contamination.

Laboratory 9325B

In the period between reporting their results and the release of the tables of results to the participants, Laboratory 9325B had continued with further method development. Their original results were reported with 2 significant figures and no decimals. By the time the table of results were released, they had improved confidence in their method and were reporting values to 3 significant figures (1 decimal place). They resubmitted their original results calculated to 3 significant figures. Both sets of values are in Tables 1-4, with the original reported values enclosed in brackets. The revised values were used for the statistical calculations and plotted on the Youden graphs.

Laboratory 9325B had a broad range of results relative to the target for the Injection-Ready solutions (OC1 and OC2). While 50% of their results were within 90-110% of the target, almost 30% of their results were outside the range of ±20% of the target (Table 6 and Figure 35). Within-laboratory precision was variable. Results were close to or on the diagonal line for o,p-DDT (Figure 7), γ-Chlordane (Figure 17), Methoxychlor (Figure 21), and HCB (Figure 25). Results for data pairs of the other parameters varied, with one result close to the target, but the second result biased high or low. Most commonly the result for OC2 was closer to the target than the result for OC1, suggesting possible intercept problems.

Their results for the solutions processed through Clean-up (OC3 and OC4) suggest that some contamination was present in the Clean-up materials, as 43% of their results are >130% of the target values (Table 6 and Figure 36). This appears to have particularly affected the lower concentration level solution (OC3), as all of the results are biased high from the interlaboratory mean, except for Endosulfan I. However Endosulfan I was not detected in OC1, while a result was reported for OC3. In the overview above, Laboratory 9325B was flagged as erratic for almost all the parameters. One source of this erratic performance may be the contamination in OC3.

The variability in the results for the low concentration solutions (OC1 and OC3) suggest that the MSD detector used for this set of analyses (Table 5) is not sufficiently sensitive at the target levels of this study. Further development work is required to improve the sensitivity of this technique.

Laboratory 9325C

Ninety percent of Laboratory 9325C's results for OC1 and OC2 were within 80-110% of the target. This corresponds to the results reported as "9325A", as the same calibration standards were used and the new Clean-up procedure does not affect the analysis of the injection-ready solutions. They demonstrated good within-laboratory precision except for p,p-DDT (Figure 5), o,p-DDT (Figure 7), p,p-DDD (Figure 9), p,p-DDE (Figure 13), Methoxychlor (Figure 21), and HCB (Figure 25). These parameters demonstrated a tendency to a possible slope problem, as they had good agreement with the target at the low concentration (OC1), but were biased slightly low at the high concentration (OC2). However Methoxychlor appears to have a more severe slope problem, as the result for OC2 was 66.7% of the target.

The results for the ampoules processed through Clean-up (OC3 and OC4) show a shift in the results, as only 2 results (7%) were less than 90% of the target, and 30% of

the results are greater than 120% of the target (Table 6 and Figure 36). All but two of the results reported in OC3 and OC4 were greater than the corresponding results in OC1 and OC2. Methoxychlor was not detected in OC3 and p,p-DDT remained the same between OC1 and OC3. These results suggest that their Clean-up procedure adds an interferant to the sample. They should confirm that the column packing material is properly pretreated prior to use in the Clean-up stage, to avoid possible contamination.

Laboratory 9325 indicated with their original submission of results that the GC/ECD with "dry-packed" Florisil Clean-up was their old method, and that the GC/MSD with "wet-packed" Florisil Clean-up was going to be their new method. At the time of this interlaboratory study, the results suggest that further development work was required before changing procedures. The new GC/MSD method does not appear to be as sensitive at lower concentrations, nor was consistent within-laboratory performance achieved.

The submission of the third set of results ("C") reflected a change in the Clean-up procedure, by having all the target compounds collected in one solution instead of two separate fractions (Table 5). As noted above, there was a high bias relative to the target for many of the compounds in the "C" data set, which did not occur with the old procedure ("A" data set). The "wet" packing may be introducing some contamination from the solvent. Laboratory 9325 should ensure that all solvents are pure and free of contaminants prior to use in the Clean-up stage. No co-elution problems were noted with the submission of the third set of results. However some interferants that may have been in the "other" fraction may now be causing some quantitation errors of target compounds in the single fraction analysis. Care must be taken that co-elution problems are not occurring.

Laboratory 9326

Laboratory 9326 noted with their results that o,p-DDT, which is not on their target list, may be interfering with p,p-DDD (on their target list). For OC1 and OC2, the presence of both compounds in the solutions has caused a high bias in their results. The reported value for p,p-DDD has been excluded from the statistical calculations, due to this interferant. Laboratory 9326 should consider adding o,p-DDT to their target list and reporting a combined result for the two compounds, as reporting a value for only p,p-DDD in a real sample may be resulting a biased high data set, if o,p-DDT is also present and not accounted for.

Fifty percent of the results for OC1 and OC2 were in the 90-110% range of the target (Table 6 and Figure 35). As well as the identified high bias for p,p-DDD, they were also biased high for α-Chlordane (Figure 15) and HCB (Figure 25). Within-laboratory precision could be improved, as several data points were closer to one of the quadrant-dividing lines than to the diagonal line (Figures 1, 13, 17, and 25).

As noted in the overview above, Laboratory 9326 was biased high for α-Chlordane in the Injection-Ready Solutions (OC1 and OC2), but had good agreement with the target in the Ampoules processed through Clean-up (OC3 and OC4). Two possible reasons for this are analysis on different days, thereby suggesting different calibration between the days, or loss of α-Chlordane during the Clean-up process.

Laboratory 9326 also explained that in the two fractions from the Clean-up obtained for OC3 and OC4, an unknown compound in their Hexane fraction had the same GC

retention time as p,p-DDD. Their method development experiments had shown that p,p-DDD is found only in their 40% Dichloromethane/Hexane fraction. They noted that if any of the unknown carries over into the second fraction, their p,p-DDD result will be biased high. This "unknown compound" is most probably o,p-DDT, which should have been separated from p,p-DDD by the Clean-up process. Laboratory 9326's result for OC4 was biased higher than the other participants (Table 4), suggesting some interference from o,p-DDT. However two other participants had higher values for OC3 than Laboratory 9326 (Table 3), placing Laboratory 9326 within the interlaboratory grouping. Their OC3 result was 124% of the target and the OC4 result was 118% of the target, 75-80% separation of o,p-DDT and p,p-DDD appears to have taken place in the Clean-up process. As these results place Laboratory 9326 within the interlaboratory grouping, their results for p,p-DDD in OC3 and OC4 were included in the statistical calculations and plotted in Figure 10. However further development work should be undertaken to more effectively separate o,p-DDT from p,p-DDD.

Almost all of the results for OC3 and OC4 fall within the range of 80-120% of the target (Table 6 and Figure 36). However erratic performance was demonstrated for α-HCH (Figure 2), γ-HCH (Figure 4), and p,p-DDT (Figure 6). The results for HCB suggest a possible slope problem, as the results for OC1 and OC3 were close to the target, but the results for OC2 and OC4 were biased high.

Laboratory 9327

Laboratory 9327 had 75% of their results for OC1 and OC2 within 90-110% of the target, and the remaining 25% were within 80-120% of the target (Table 6 and Figure 35). They had good within-laboratory precision except for p,p-DDT (Figure 5), p,p-DDD (Figure 9), Heptachlor Epoxide (Figure 19), and HCB (Figure 25). Within-laboratory precision for o,p-DDT (Figure 7), Methoxychlor (Figure 21), and Endrin (Figure 27) were borderline, but their results were within one Standard Deviation of the mean and therefore may be considered acceptable.

There was an increase in the values for several parameters in the ampoules processed through Clean-up (OC3 and OC4). A higher percentage of results were in the range 110-120% of the target and the result for o,p-DDT in OC3 was 127% of the target (Table 6 and Figure 26). It appears that the Clean-up procedure adds an interferant to some of the target parameters, particularly o,p-DDT and o,p-DDD. This does not appear to be critical at higher concentrations but may be critical at lower concentrations. Program needs of this laboratory may determine how important this problem is and whether investigation into their Clean-up materials is required.

5 CONCLUSION

The interlaboratory mean and median for the Injection-Ready solutions demonstrated good agreement with the target values (< 15% difference). Overall agreement with the target has improved from 50-60% of the results being in the range 90-110% of the target in the first study[4], to 70-80% of the results in this study being in the range 90-110% of target. Between-laboratory relative variability at the higher concentration level is similar to the first study[4] among these participants, though many parameters have improved from ± 20% to ± 10-15%. Between-laboratory variability at the lower concentration is more variable in this study than the previous study[4], suggesting that several participants have intercept problems.

The interlaboratory mean and median for the solutions processed through Clean-up also demonstrated good agreement with the target (< 15% difference), except for Heptachlor Epoxide, Methoxychlor and Endosulfan I in OC3 and Methoxychlor in OC4 (differ by 15-35%). There was no statistically significant difference between the means or variances of OC2 (no Clean-up) vs. OC4 (Clean-up) at the higher concentration level for any of the parameters ($\alpha = 0.05$). However, at the lower concentration, there was a statistically significant difference in the means between OC1 (no Clean-up) and OC3 (Clean-up) for p,p-DDD and Heptachlor Epoxide ($\alpha = 0.05$). There were statistically significant differences in the variances between OC1 and OC3 for α-HCH, γ-HCH, o,p-DDT, γ-Chlordane, Methoxychlor, HCB, Endosulfan I, and Endosulfan II ($\alpha = 0.05$). In several cases the Clean-up procedure appears to add an interferant to the solutions, while in other cases, the Clean-up procedure appears to retain some of the target analytes. This did not appear critical at the higher concentration level but may be critical at the lower concentration level. None of these problems appears to be compound-specific. Individual laboratories need to investigate the possible sources of these biases, such as contamination of the packing material, solvent used, or problems in fractionation.

The participants in this interlaboratory study demonstrate an improvement in performance from the previous interlaboratory study[4]. Individual participants may have a problem with some individual compounds that require individual attention. It is the intent to continue with future interlaboratory studies in support of the IADN program, assessing not only between-laboratory comparability for calibration and Clean-up, but to include spiked matrix samples for precipitation and ambient air to compare between-laboratory method performance.

6 REFERENCES

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7 APPENDIX 1 - RESULTS AND GRAPHS

TABLE 1 - RESULTS FOR AMPOULE 93-2-OC1
ng/mL

PARAMETER	TARGET	LABORATORY ID CODE								MEAN	MEDIAN	STD DEV	%RSD	n
AMPOULE	93-2-OC1	9322	9323A	9324	9325A	9325B	9325C	9326	9327					
α-HCH	4.03	3.9	4.39	4.10	3.4	3.5 (4)	3.4	3.0	4.2	3.736	3.7	0.482	12.9%	8
γ-HCH	4.16	3.9	4.47	4.23	3.8	3.9 (4)	3.9	3.6	4.2	4.000	3.9	0.279	7.0%	8
p,p-DDT	3.84	4.5	4.56	4.87	4.0	2.7 (3)	3.7	3.6	4.3	4.029	4.15	0.691	17.2%	8
o,p-DDT	3.84	4.6	4.33	4.37	4.2	3.8 (4)	3.9	N/A	4.2	4.200	4.2	0.276	6.6%	7
p,p-DDD	4.76	4.9	5.28	4.37	4.7	3.5 (3)	4.0	8.7 •	5.3	4.579	4.7	0.667	14.6%	7
o,p-DDD	5.04	N/A	5.30 #	6.40	N/A	N/A	N/A	N/A	4.8	5.500	5.30	0.819	14.9%	3
p,p-DDE	4.08	3.9	4.85	5.43	3.0	4.3 (4)	3.7	4.8	3.4	4.173	4.1	0.821	19.7%	8
o,p-DDE	4.84	N/A	N/A	4.57	N/A	N/A	N/A	N/A	N/A	-	-	-	-	1
α-CHLORDANE	4.56	4.6	4.90	5.52	4.5	3.7 (4)	4.5	7.9	4.9	5.065	4.75	1.255	24.8%	8
γ-CHLORDANE	4.40	4.5	4.71	5.01	4.4	4.5 (5)	4.4	4.7	4.4	4.578	4.5	0.216	4.7%	8
HEPTACHLOR EPOXIDE	4.08	4.2	4.76 #	4.92	4.3	5.2 (5)	4.4	N/A	4.2	4.569	4.4	0.394	8.6%	7
METHOXYCHLOR	3.96	4.5	5.43	5.93	4.5	3.0 (3)	3.8	N/A	4.0	4.451	4.5	0.990	22.2%	7
DIELDRIN	4.32	4.3	5.58 #	4.82	4.4	ND	4.6	4.7	3.5	3.988	4.5	1.712	42.9%	8
HEXACHLOROBENZENE	4.24	4.6	4.22	4.72	3.9	3.6 (4)	4.3	4.7	3.9	4.243	4.26	0.417	9.8%	8
ENDRIN	4.48	4.9	4.55	4.93	N/A	N/A	N/A	N/A	4.7	4.770	4.8	0.179	3.7%	4
ENDOSULFAN I	4.64	6.2	5.17	5.52	5.3	ND	5.2	N/A	4.6	4.570	5.25	2.071	45.3%	7
ENDOSULFAN II	4.04	4.2	5.37	5.47	4.2	ND	4.4	N/A	4.4	4.006	4.4	1.846	46.1%	7
OXYCHLORDANE	5.84	N/A	5.76 #	7.38	5.4	9.4 (9)	5.0	N/A	N/A	6.588	5.76	1.813	27.5%	5

\# Results reported from DB-17 column (confirmatory column) for those results with non-optimal resolution on DB-5 column.

• Result includes co-elutant, possibly o,p-DDT (not on routine target list). Value not included in statistical calculations.

TABLE 2 - RESULTS FOR AMPOULE 93-2-OC2
ng/mL

PARAMETER	TARGET	LABORATORY ID CODE								MEAN	MEDIAN	STD DEV	%RSD	n
AMPOULE	93-2-OC2	9322	9323A	9324	9325A	9325B	9325C	9326	9327					
α-HCH	20.14	21.8	21.99	16.96	19.4	20.0 (20)	18.0	18.6	20.7	19.681	19.7	1.790	9.1%	8
γ-HCH	20.80	21.4	22.73	17.39	20.6	20.8 (21)	19.3	19.6	20.6	20.303	20.6	1.581	7.8%	8
p,p-DDT	19.20	23.7	22.00	21.39	20.5	18.9 (19)	16.4	18.8	17.2	19.861	19.7	2.483	12.5%	8
o,p-DDT	19.20	24.1	21.98	18.58	19.8	18.7 (19)	17.0	N/A	19.7	19.980	19.7	2.365	11.8%	7
p,p-DDD	23.80	29.3	26.49	25.22	24.0	22.9 (23)	17.7	38.7 •	23.8	24.201	24.0	3.569	14.7%	7
o,p-DDD	25.20	N/A	27.18 #	21.49	N/A	N/A	N/A	N/A	22.0	23.557	22.0	3.148	13.4%	3
p,p-DDE	20.40	24.2	23.61	18.28	17.5	17.1 (17)	16.5	21.2	19.1	19.686	18.69	2.976	15.1%	8
o,p-DDE	24.20	N/A	N/A	21.99	N/A	N/A	N/A	N/A	N/A	-	-	-	-	1
α-CHLORDANE	22.60	25.9	24.65	19.40	21.2	21.9 (22)	23.7	36.6	23.2	24.569	23.45	5.269	21.4%	8
γ-CHLORDANE	22.00	26.5	24.07	19.74	21.0	21.5 (21)	22.8	21.6	21.6	22.351	21.6	2.100	9.4%	8
HEPTACHLOR EPOXIDE	20.40	24.6	25.57 #	19.20	20.3	22.1 (22)	19.9	N/A	18.9	21.510	20.3	2.664	12.4%	7
METHOXYCHLOR	19.80	25.2	26.11	27.74	21.5	15.5 (16)	13.2	N/A	16.8	22.142	21.5	5.745	25.9%	7
DIELDRIN	21.60	25.1	29 14	19.14	21.7	20.9 (21)	21.0	21.3	18.2	22.060	21.15	3.504	15.9%	8
HEXACHLOROBENZENE	21.20	25.9	21.83	19.46	18.4	19.3 (19)	17.4	28.0	21.9	21.524	20.645	3.728	17.3%	8
ENDRIN	22.40	27.3	22.83	19.38	N/A	N/A	N/A	N/A	20.7	22.553	21.765	3.469	15.4%	4
ENDOSULFAN I	23.20	36.7	26.15	21.59	25.3	21.5 (21)	23.6	N/A	22.4	25.320	23.6	5.326	21.0%	7
ENDOSULFAN II	20.20	24.6	27.23	21.93	19.9	16.2 (16)	19.4	N/A	19.4	21.237	19.9	3.688	17.4%	7
OXYCHLORDANE	29.20	N/A	29.55	28.02	24.6	26.1 (26)	25.1	N/A	N/A	26.674	26.1	2.073	7.8%	5

\# Results reported from DB-17 column (confirmatory column) for those results with non-optimal resolution on DB-5 column.

• Result includes co-elutant, possibly o,p-DDT (not on routine target list). Value not included in statistical calculations.

TABLE 3 - RESULTS FOR AMPOULE 93-2-OC3
ng/mL

PARAMETER	TARGET	LABORATORY ID CODE									MEAN	MEDIAN	STD DEV	%RSD	n
AMPOULE	93-2-OC3	9322	9323A	9323B	9324	9325A	9325B	9325C	9326	9327					
α-HCH	4.03	4.0	4.14	3.98	3.90	3.5	7.0 (7)	3.7	2.8	4.6	4.180	3.98	1.166	27.9%	9
γ-HCH	4.16	4.0	3.93	3.82	3.99	3.8	8.2 (8)	4.1	3.4	4.4	4.404	3.99	1.448	32.9%	9
p,p-DDT	3.84	5.0	3.45	3.97	4.48	4.2	6.6 (7)	3.7	3.5	4.3	4.356	4.2	0.976	22.4%	9
o,p-DDT	3.84	5.1	3.37	3.68	4.42	2.2	6.1 (6)	4.3	N/A	4.9	4.259	4.36	1.189	27.9%	8
p,p-DDD	4.76	5.0	4.75	4.79	6.19	4.9	7.6 (8)	4.1	5.9	5.3	5.392	5.0	1.038	19.2%	9
o,p-DDD	5.04	N/A	4.49	4.38	5.16	N/A	N/A	N/A	N/A	5.6	4.908	4.825	0.576	11.7%	4
p,p-DDE	4.08	4.7	4.31	4.57	4.67	3.4	7.0 (7)	4.5	4.5	3.5	4.572	4.5	1.032	22.6%	9
o,p-DDE	4.84	N/A	N/A	N/A	5.79	N/A	N/A	N/A	N/A	N/A	-	-	-	-	1
α-CHLORDANE	4.56	4.7	3.91	3.83	4.74	4.8	7.9 (8)	5.0	4.7	5.2	4.976	4.74	1.188	23.9%	9
γ-CHLORDANE	4.40	4.6	4.41	4.15	4.83	4.6	7.7 (8)	4.7	4.2	4.9	4.899	4.6	1.082	22.1%	9
HEPTACHLOR EPOXIDE	4.08	4.6	4.28	4.33	4.76	4.7	6.1 (6)	5.3	N/A	4.8	4.859	4.73	0.592	12.2%	8
METHOXYCHLOR	3.96	5.0	6.30	6.58	5.63	4.4	5.8 (6)	ND	N/A	4.4	4.764	5.315	2.087	43.8%	8
DIELDRIN	4.32	4.5	4.91	5.53	4.39	4.6	10.7 (11)	5.2	3.7	4.2	5.303	4.6	2.095	39.5%	9
HEXACHLOROBENZENE	4.24	5.0	3.82	4.03	4.94	3.6	6.7 (7)	5.6	4.4	3.5	4.621	4.4	1.053	22.8%	9
ENDRIN	4.48	5.1	4.90	5.04	4.25	N/A	N/A	N/A	N/A	5.0	4.858	5.0	0.348	7.2%	5
ENDOSULFAN I	4.64	6.5	4.75	5.10	5.06	5.7	5.1 (5)	6.1	N/A	5.0	5.414	5.1	0.617	11.4%	8
ENDOSULFAN II	4.04	4.2	5.08	5.28	N/A	4.2	6.5 (6)	4.7	N/A	4.3	2.694	4.7	0.828	30.7%	7
OXYCHLORDANE	5.84	N/A	5.19	5.04	6.98	5.9	7.3 (7)	5.6	N/A	N/A	6.002	5.75	0.838	15.6%	6

NOTE: Laboratory 9323 did duplicate Clean-up for Ampoules 93-2-OC3 and 93-2-OC4, using the same procedure. The results have been reported as "9323A" and "9323B"

TABLE 4 - RESULTS FOR AMPOULE 93-2-OC4
ng/mL

PARAMETER	TARGET	LABORATORY ID CODE									MEAN	MEDIAN	STD DEV	%RSD	n
AMPOULE	93-2-OC4	9322	9323A	9323B	9324	9325A	9325B	9325C	9326	9327					
α-HCH	20.14	24.1	20.97	22.93	16.48	19.8	17.3 (17)	19.5	24.8	19.0	20.542	19.8	2.909	14.2%	9
γ-HCH	20.80	23.4	20.02	22.64	16.62	21.3	19.8 (20)	21.8	23.5	19.5	20.953	21.3	2.215	10.6%	9
p,p-DDT	19.20	24.0	20.42	23.06	20.44	22.3	17.9 (18)	20.6	21.5	17.7	20.880	20.6	2.132	10.2%	9
o,p-DDT	19.20	25.4	18.84	20.92	20.71	16.0	17.3 (17)	21.6	N/A	19.1	19.984	19.905	2.891	14.5%	8
p,p-DDD	23.80	25.3	22.71	26.06	24.88	25.7	20.3 (20)	22.2	28.2	23.0	24.261	24.88	2.404	9.9%	9
o,p-DDD	25.20	N/A	21.70	24.82	21.19	N/A	N/A	N/A	N/A	22.2	22.478	21.95	1.615	7.2%	4
p,p-DDE	20.40	25.5	21.11	23.37	20.49	17.0	18.6 (19)	21.0	22.0	17.5	20.730	21.0	2.750	13.3%	9
o,p-DDE	24.20	N/A	N/A	N/A	25.10	N/A	N/A	N/A	N/A	N/A	-	-	-	-	1
α-CHLORDANE	22.60	26.2	20.70	23.13	18.92	24.9	18.4 (18)	29.5	23.1	23.0	23.094	23.1	3.520	15.2%	9
γ-CHLORDANE	22.00	26.4	20.40	23.49	19.46	24.1	18.6 (19)	23.6	21.0	22.1	22.128	22.1	2.500	11.3%	9
HEPTACHLOR EPOXIDE	20.40	24.6	18.52	21.82	19.27	23.9	17.3 (17)	25.1	N/A	19.7	21.276	20.76	2.994	14.1%	8
METHOXYCHLOR	19.80	24.1	24.97	28.68	26.19	24.1	17.2 (17)	18.6	N/A	17.3	22.643	24.1	4.362	19.3%	8
DIELDRIN	21.60	25.1	23.17	25.88	17.85	24.6	23.0 (23)	26.0	19.3	18.3	22.578	23.17	3.259	14.4%	9
HEXACHLOROBENZENE	21.20	29.4	17.90	21.40	21.28	17.8	18.6 (19)	24.5	26.7	19.1	21.853	21.28	4.156	19.0%	9
ENDRIN	22.40	24.9	21.29	24.60	17.51	N/A	N/A	N/A	N/A	20.2	21.700	21.3	3.107	14.3%	5
ENDOSULFAN I	23.20	37.4	21.98	24.02	20.57	29.6	23.4 (23)	29.7	N/A	22.6	26.159	23.71	5.661	21.6%	8
ENDOSULFAN II	20.20	23.0	23.04	26.53	N/A	22.2	13.6 (14)	24.8	N/A	19.0	21.739	23.0	4.273	19.7%	7
OXYCHLORDANE	29.20	N/A	25.34	27.27	26.75	29.9	22.6 (23)	27.1	N/A	N/A	26.493	26.925	2.414	9.1%	6

NOTE: Laboratory 9323 did duplicate Clean-up for Ampoules 93-2-OC3 and 93-2-OC4, using the same procedure. The results have been reported as "9323A" and "9323B".

TABLE 5 - INSTRUMENTS, GC COLUMNS AND Clean-up CONDITIONS

Laboratory	Instrument & Detector	GC Column	Clean-up Conditions			
			Sample Volume	Solvents Used	Column Packing Material	Final Sample Volume
9322	HP5890 with Dual ECD	DB-1 & DB-5	1 mL	Fraction 1: Hexane Fraction 2: Hexane - Dichloromethane (1:1)	3% Silica Gel	1 mL
9323A & B	HP 5890 with Dual ECD	DB-5, 60 m & DB-17, 30 m	0.5 cm^3	Fraction 1: Hexane Fraction 2: 15% Dichloromethane - 85% Hexane Fraction 3: 60% Dichloromethane - 40% Hexane	Florisil (3% water deactivated)	1.0 cm^3
9324	Varian 3600 with ECD	DB-5, 60 m	5 mL	Hexane and Dichloromethane	1.2% Deactivated Florisil	5 mL
9325A	HP 5890 with Dual ECD	DB-1701, 60 m & DB-5, 60 m	1.0 mL	Fraction 1: Hexane Fraction 2: Dichloromethane	Florisil, 100/200 mesh, "dry packed"	5.0 mL
9325B	HP 5890 with HP 5971A MSD	HP-1, 50 m	1.0 mL	Dichloromethane	Florisil, 100/200 mesh, "wet packed"	1.0 mL
9325C	HP 5890 with Dual ECD; single fraction analysis	DB-1701, 60 m & DB-5, 60 m	1.0 mL	Dichloromethane	Florisil, 100/200 mesh, "wet packed in Hexane"	OC3 - 6.0 mL OC4 - 5.0 mL
9326	HP 5890 with ECD	DB-5, 30 m	1.5 mL	Fraction 1: Hexane Fraction 2: 40% Dichloromethane in Hexane	3% Deactivated Silica Gel, 100/200 mesh	1 mL
9327	HP 5890 with Dual ECD	DB-1, 30 m & DB-5, 30 m	1 mL	Fraction 1: Hexane Fraction 2: Hexane - Dichloromethane (50:50)	Florisil	1 mL

TABLE 6 - DISTRIBUTION OF PARTICIPANTS' RESULTS RELATIVE TO TARGET

LAB ID CODE	9322		9323A		9323B		9324		9325A		9325B		9325C		9326		9327	
Target Range	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%
	Injection-Ready Ampoules (OC1 and OC2)																	
<70%	0	0.0%	0	0.0%			0	0.0%	0	0.0%	3	10.0%	1	3.3%	0	0.0%	0	0.0%
70-80%	0	0.0%	0	0.0%			0	0.0%	1	3.3%	4	13.3%	1	3.3%	1	5.6%	0	0.0%
80-90%	0	0.0%	0	0.0%			8	22.2%	4	13.3%	6	20.0%	9	30.0%	1	5.6%	6	18.8%
90-100%	4	13.3%	2	5.9%			8	22.2%	12	40.0%	12	40.0%	10	33.3%	6	33.3%	12	37.5%
100-110%	9	30.0%	14	41.2%			4	11.1%	11	36.7%	3	10.0%	8	26.7%	3	16.7%	12	37.5%
110-120%	6	20.0%	11	32.4%			7	19.4%	2	6.7%	0	0.0%	1	3.3%	2	11.1%	2	6.3%
120-130%	9	30.0%	2	5.9%			5	13.9%	0	0.0%	1	3.3%	0	0.0%	0	0.0%	0	0.0%
>130%	2	6.7%	5	14.7%			4	11.1%	0	0.0%	1	3.3%	0	0.0%	5	27.8%	0	0.0%
	Ampoules for Analytical Clean-up (OC3 and OC4)																	
LAB ID CODE	9322		9323A		9323B		9324		9325A		9325B		9325C		9326		9327	
Target Range	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%
<70%	0	0.0%	0	0.0%	0	0.0%	0	0.0%	1	3.3%	1	3.3%	1	3.3%	1	5.6%	0	0.0%
70-80%	0	0.0%	0	0.0%	0	0.0%	2	5.9%	0	0.0%	1	3.3%	0	0.0%	0	0.0%	0	0.0%
80-90%	0	0.0%	8	23.5%	3	8.8%	6	17.6%	6	20.0%	7	23.3%	1	3.3%	3	16.7%	6	18.8%
90-100%	2	6.7%	11	32.4%	7	20.6%	5	14.7%	2	6.7%	4	13.3%	8	26.7%	3	16.7%	11	34.4%
100-110%	6	20.0%	10	29.4%	13	38.2%	11	32.4%	12	40.0%	3	10.0%	6	20.0%	4	22.2%	5	15.6%
110-120%	11	36.7%	2	5.9%	5	14.7%	7	20.6%	6	20.0%	0	0.0%	5	16.7%	4	22.2%	9	28.1%
120-130%	5	16.7%	2	5.9%	2	5.9%	0	0.0%	3	10.0%	1	3.3%	6	20.0%	3	16.7%	1	3.1%
>130%	6	20.0%	1	2.9%	4	11.8%	3	8.8%	0	0.0%	13	43.3%	3	10.0%	0	0.0%	0	0.0%

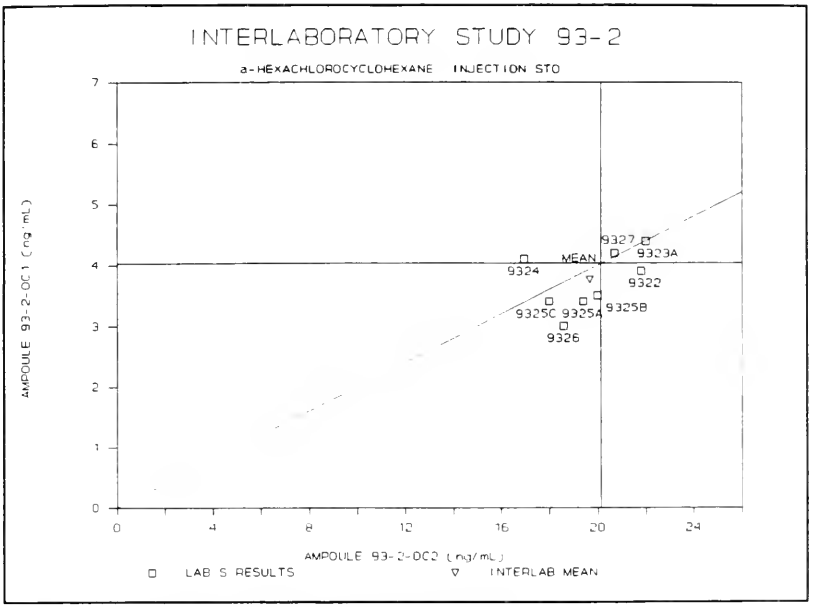

Figure 1 - *α*-HCH from Injection-Ready Ampoules

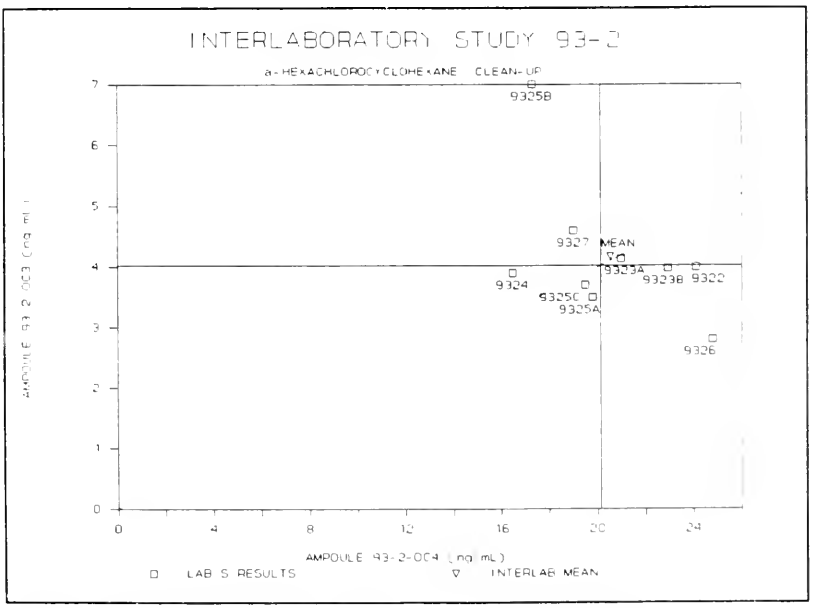

Figure 2 - *α*-HCH from Ampoules Processed Through Clean-up

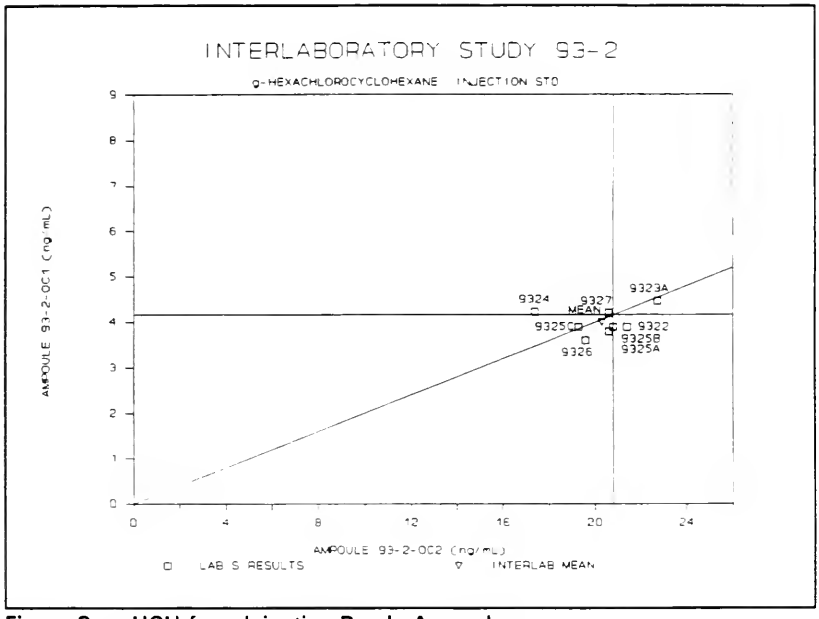

Figure 3 - *y*-HCH from Injection-Ready Ampoules

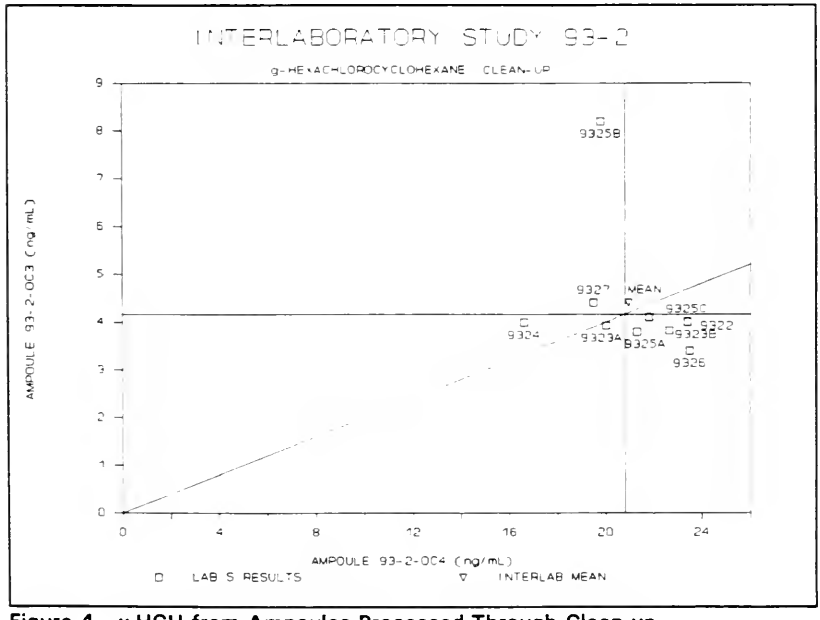

Figure 4 - *y*-HCH from Ampoules Processed Through Clean-up

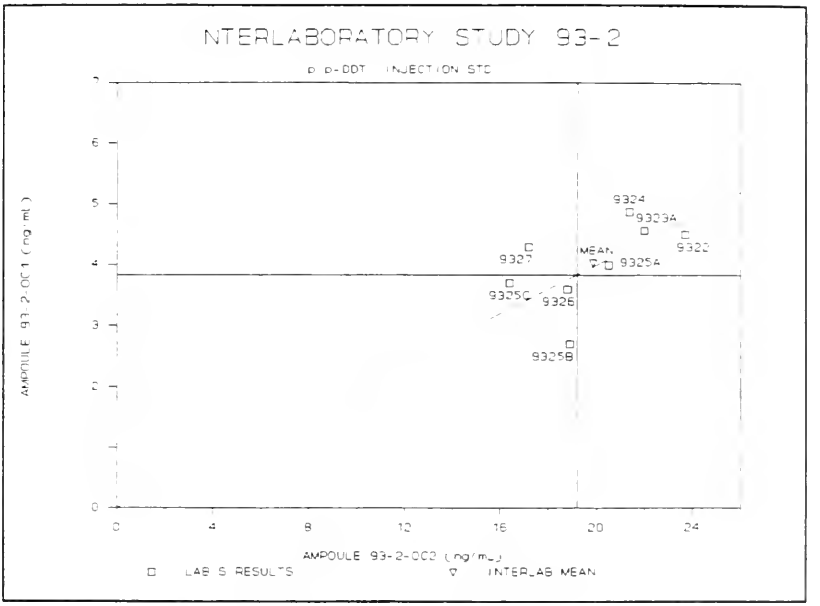

Figure 5 - p,p-DDT from Injection-Ready Ampoules

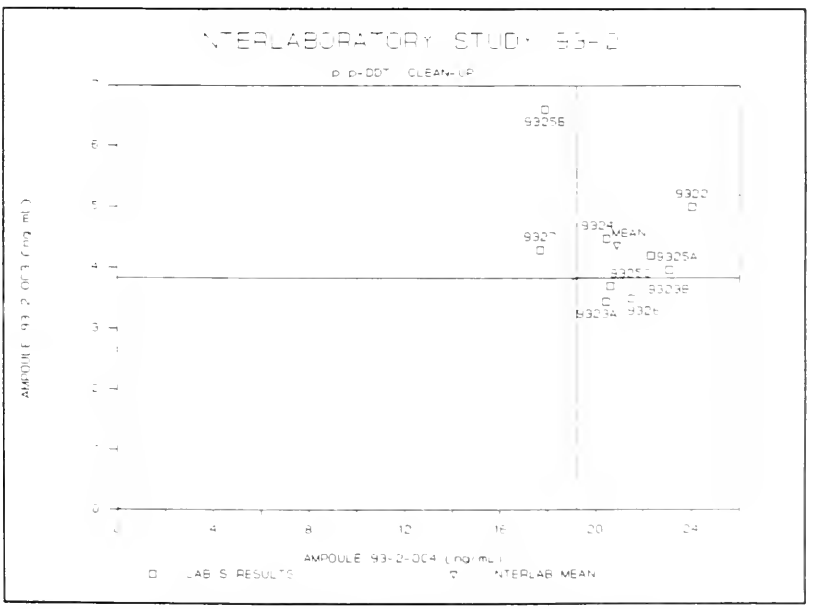

Figure 6 - p,p-DDT from Ampoules Processed Through Clean-up

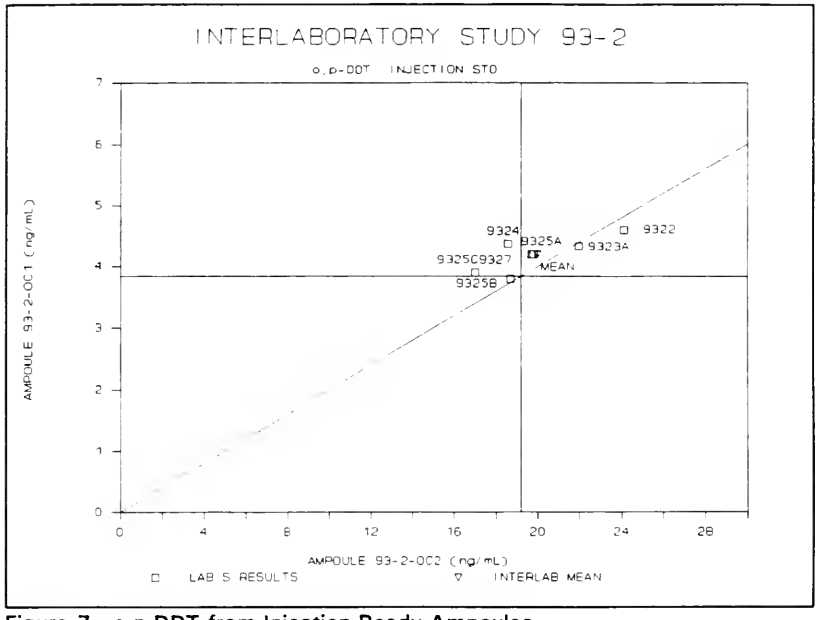

Figure 7 - o,p-DDT from Injection-Ready Ampoules

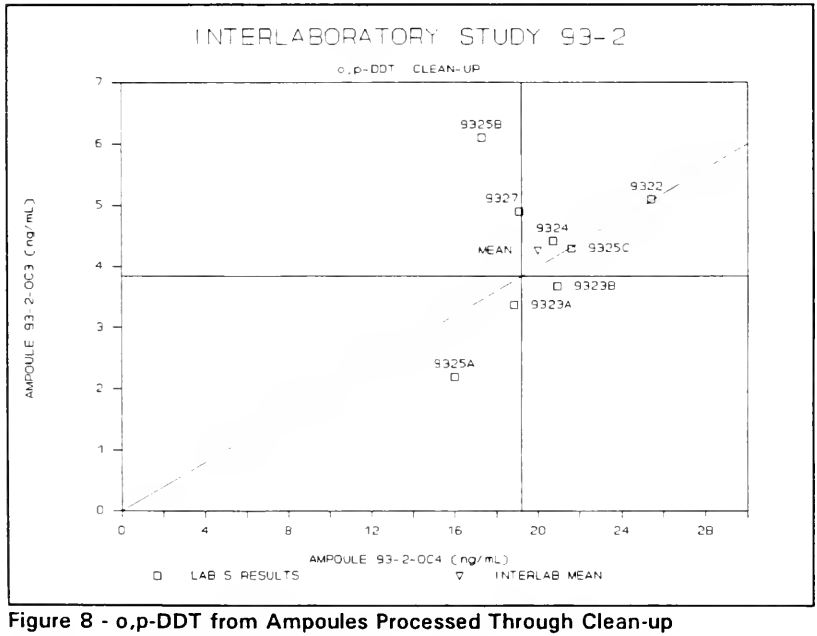

Figure 8 - o,p-DDT from Ampoules Processed Through Clean-up

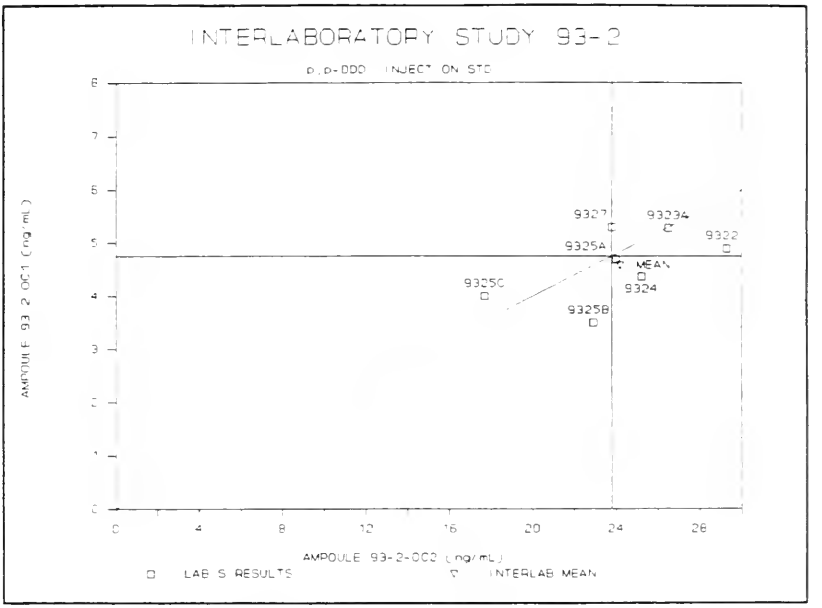

Figure 9 - p,p-DDD from Injection-Ready Ampoules

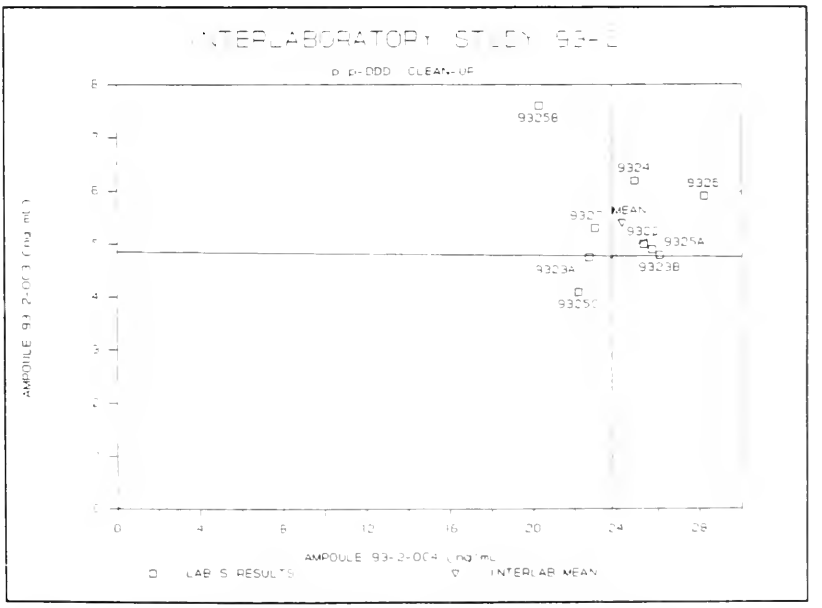

Figure 10 - p,p-DDD from Ampoules Processed Through Clean-up

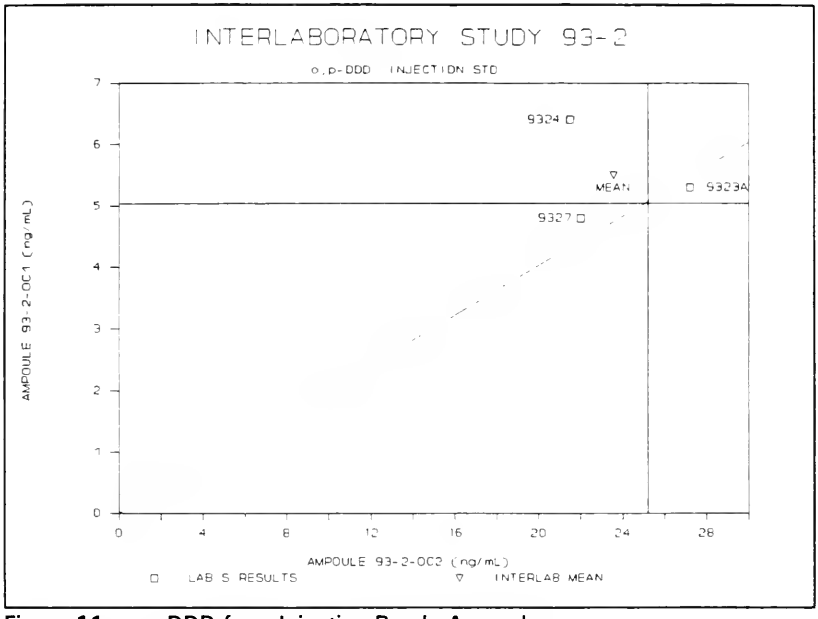

Figure 11 - o,p-DDD from Injection-Ready Ampoules

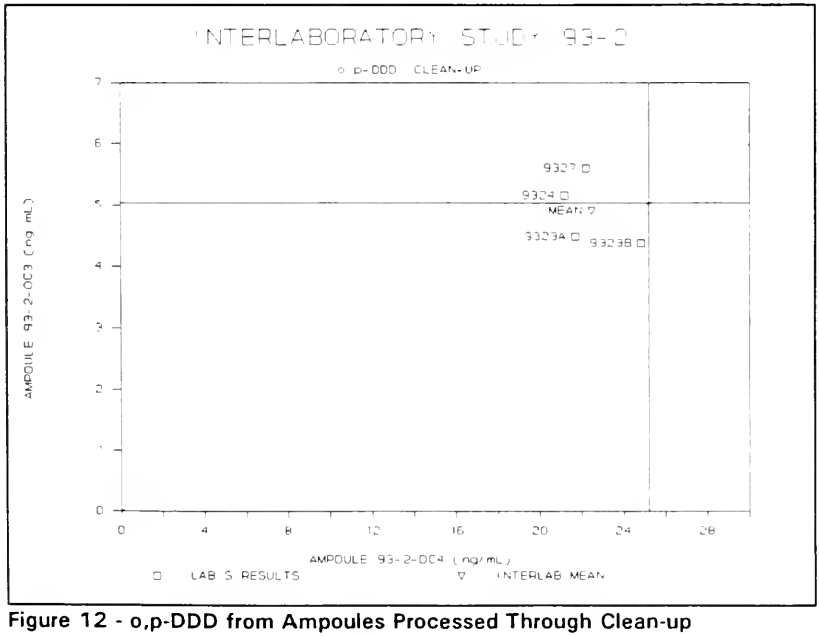

Figure 12 - o,p-DDD from Ampoules Processed Through Clean-up

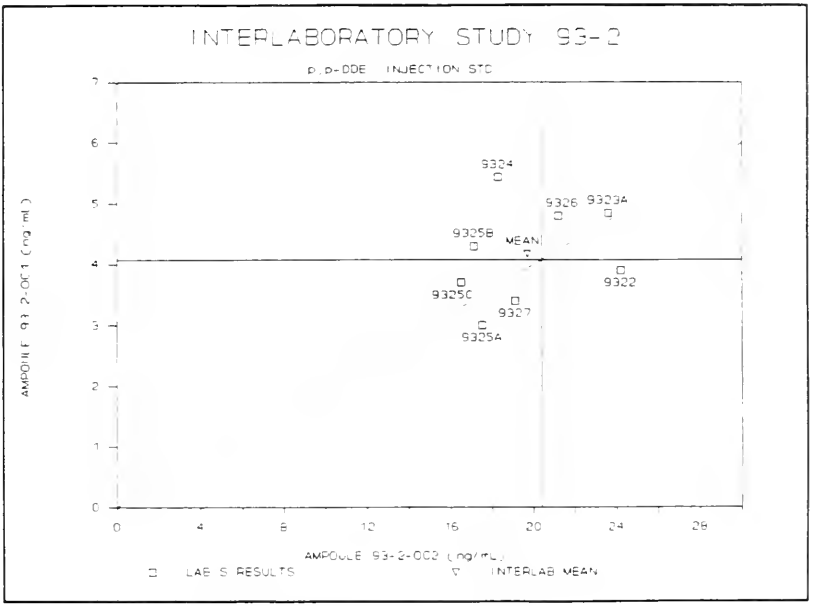

Figure 13 - p,p-DDE from Injection-Ready Ampoules

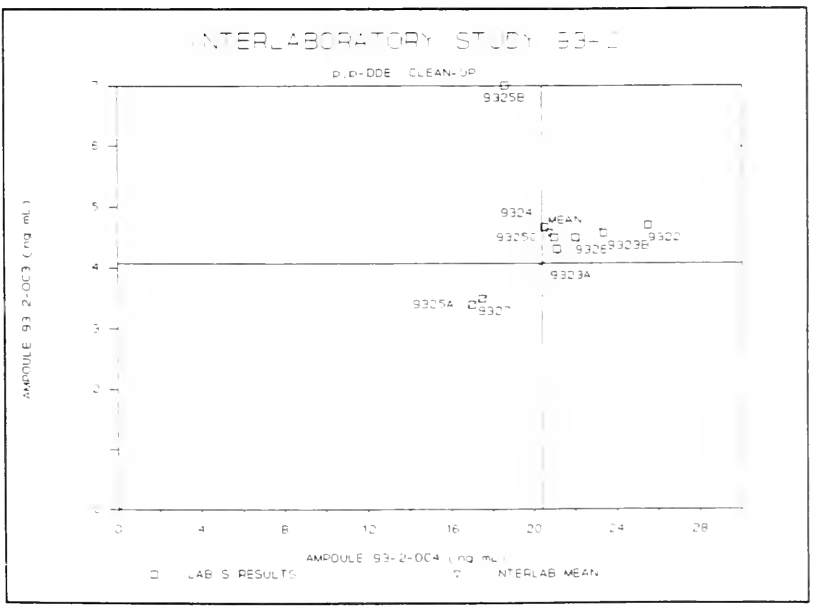

Figure 14 - p,p-DDE from Ampoules Processed Through Clean-up

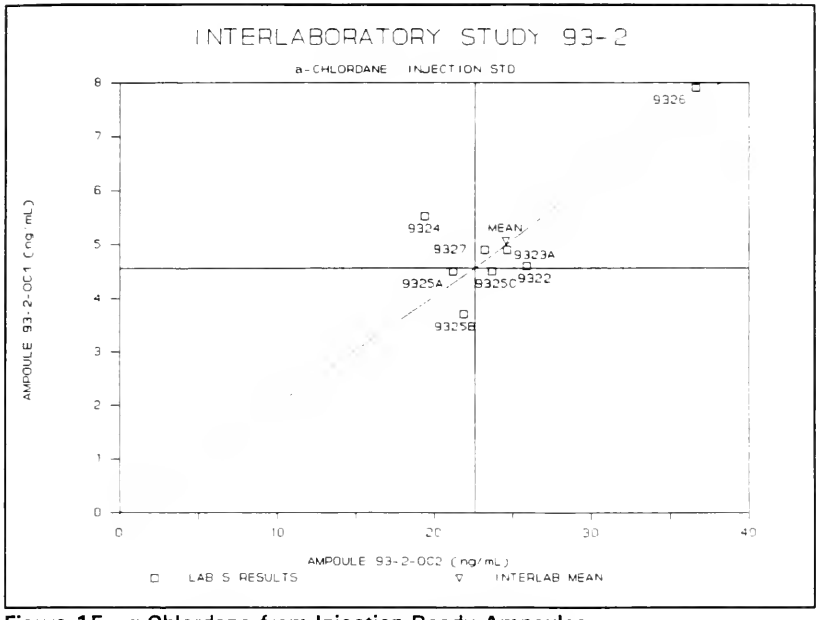

Figure 15 - *α*-Chlordane from Injection-Ready Ampoules

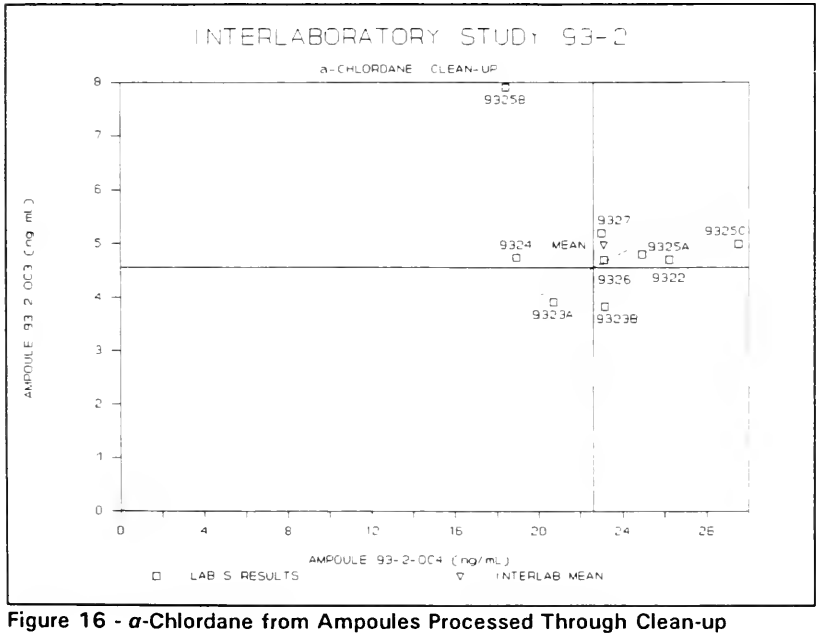

Figure 16 - *α*-Chlordane from Ampoules Processed Through Clean-up

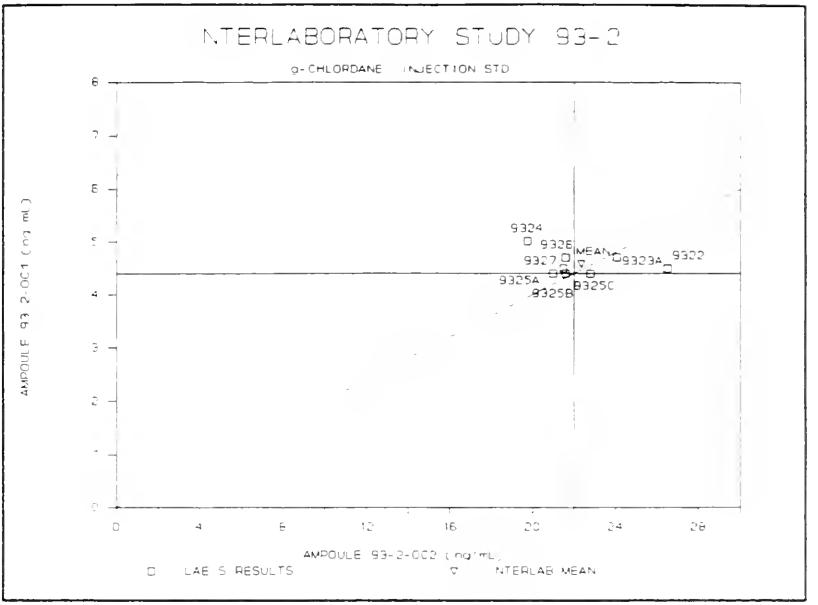

Figure 17 - *γ*-Chlordane from Injection-Ready Ampoules

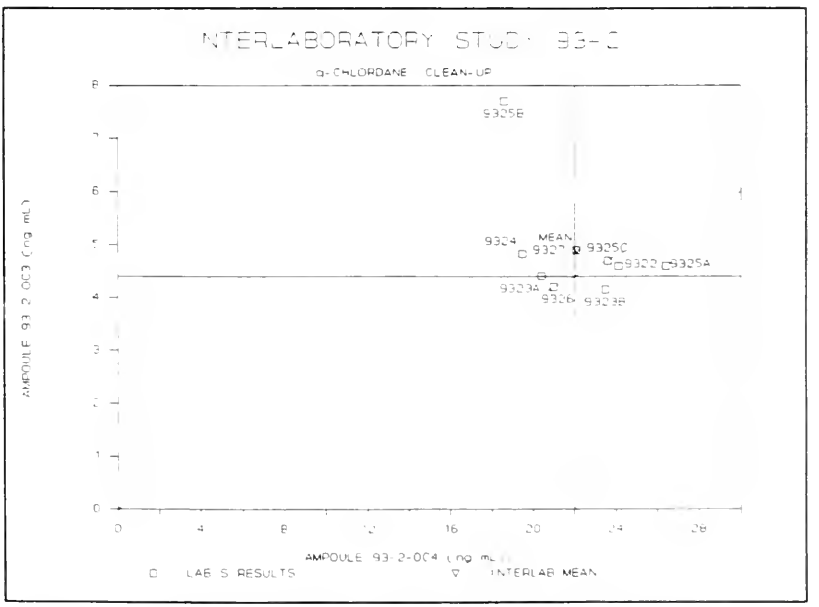

Figure 18 - *γ*-Chlordane from Ampoules Processed Through Clean-up

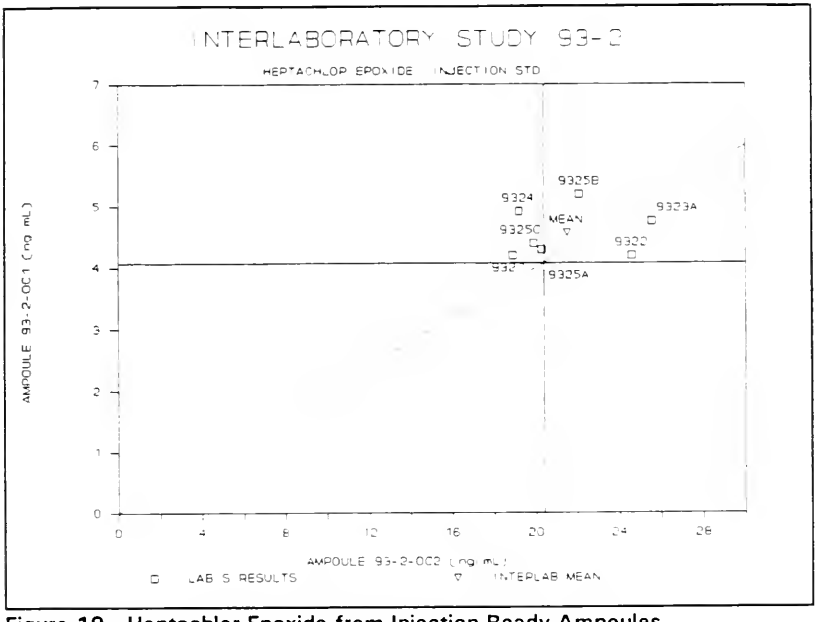

Figure 19 - Heptachlor Epoxide from Injection-Ready Ampoules

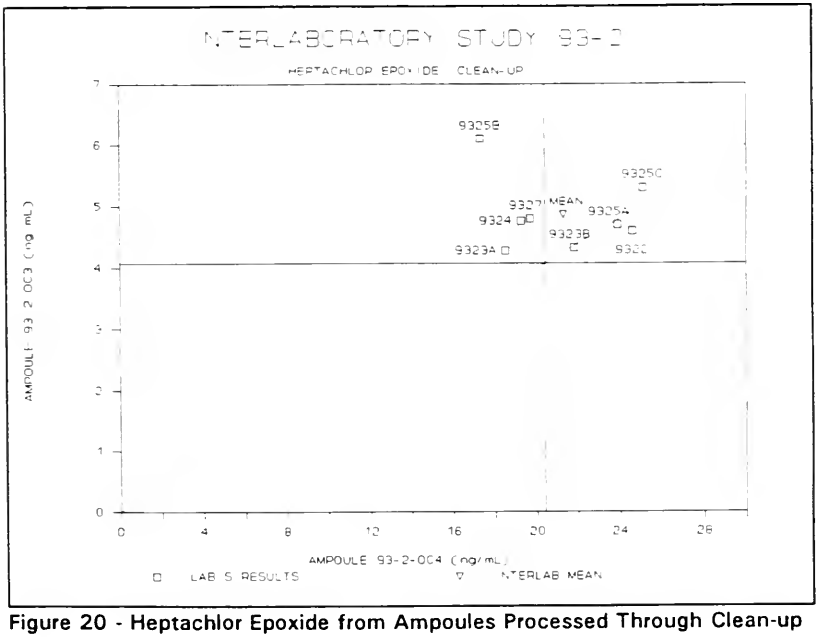

Figure 20 - Heptachlor Epoxide from Ampoules Processed Through Clean-up

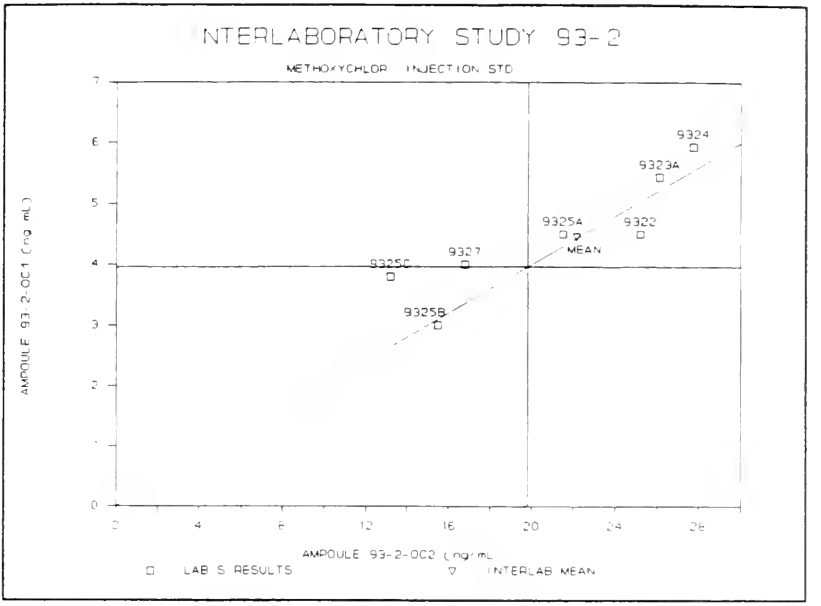

Figure 21 - Methoxychlor from Injection-Ready Ampoules

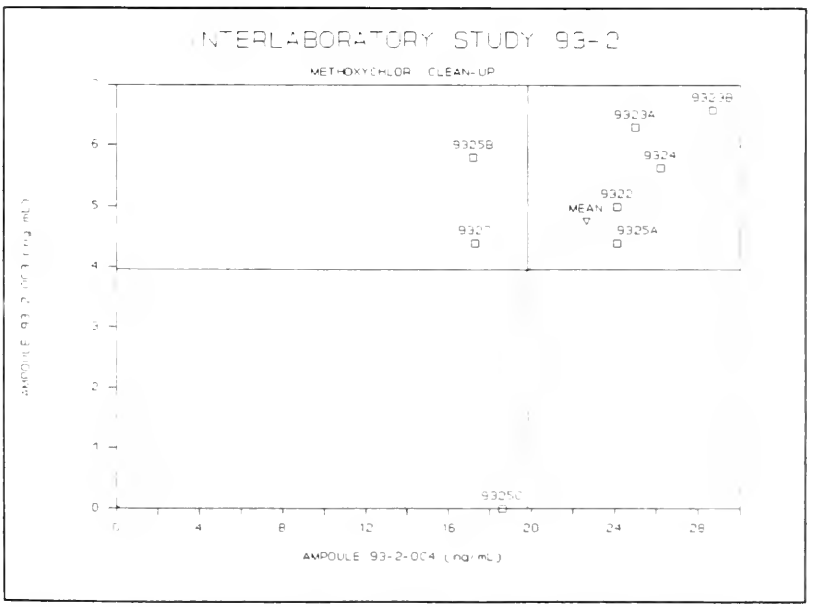

Figure 22 - Methoxychlor from Ampoules Processed Through Clean-up

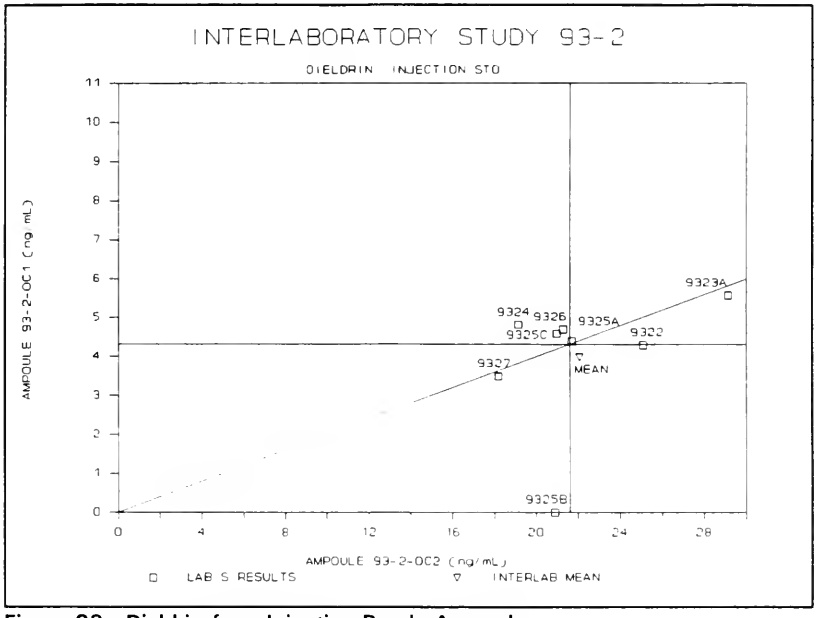

Figure 23 - Dieldrin from Injection-Ready Ampoules

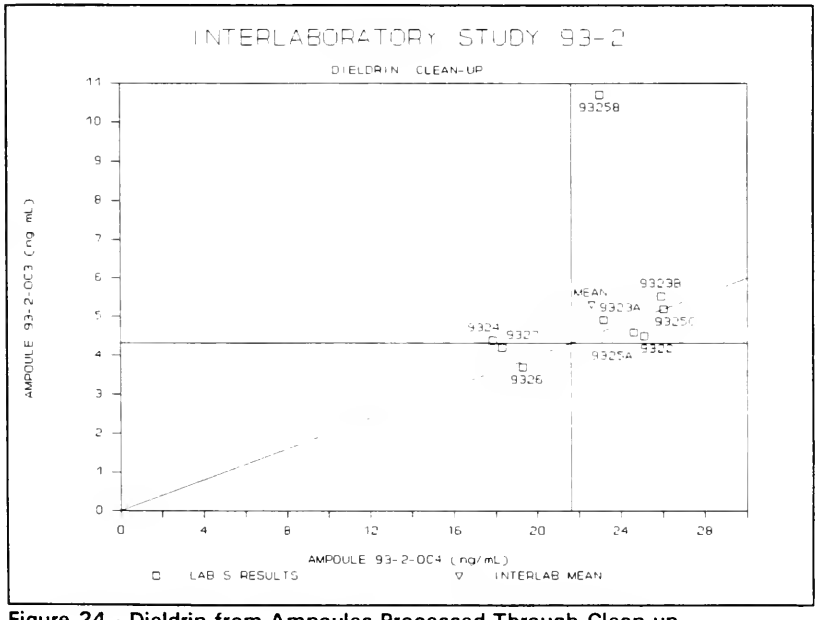

Figure 24 - Dieldrin from Ampoules Processed Through Clean-up

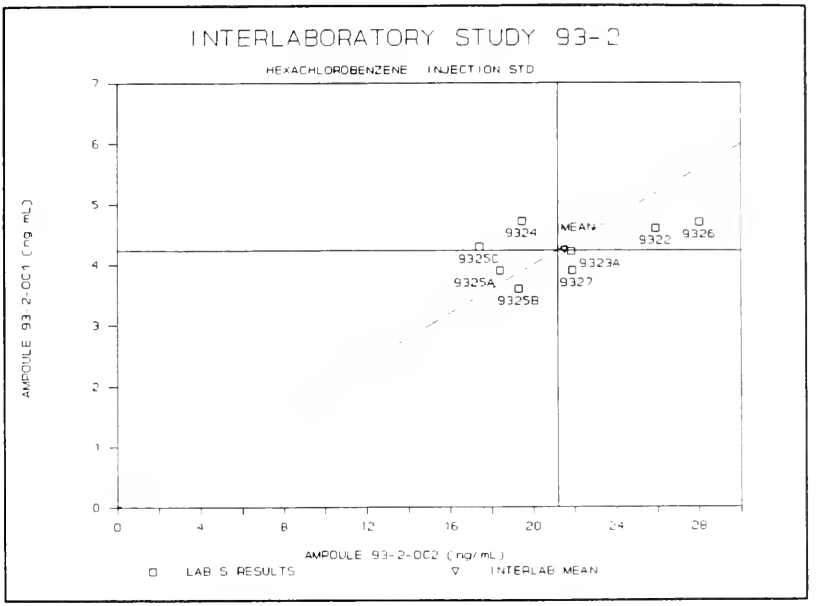

Figure 25 - Hexachlorobenzene from Injection-Ready Ampoules

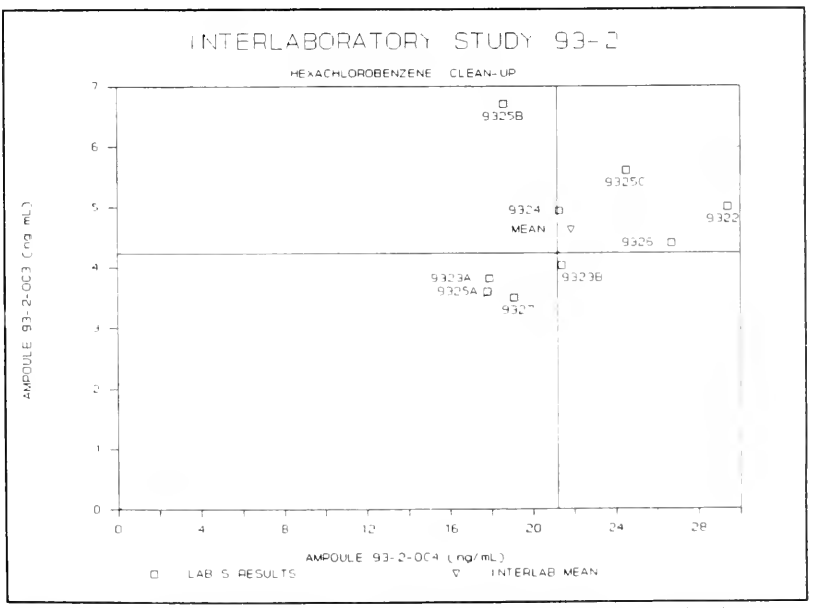

Figure 26 - Hexachlorobenzene from Ampoules Processed Through Clean-up

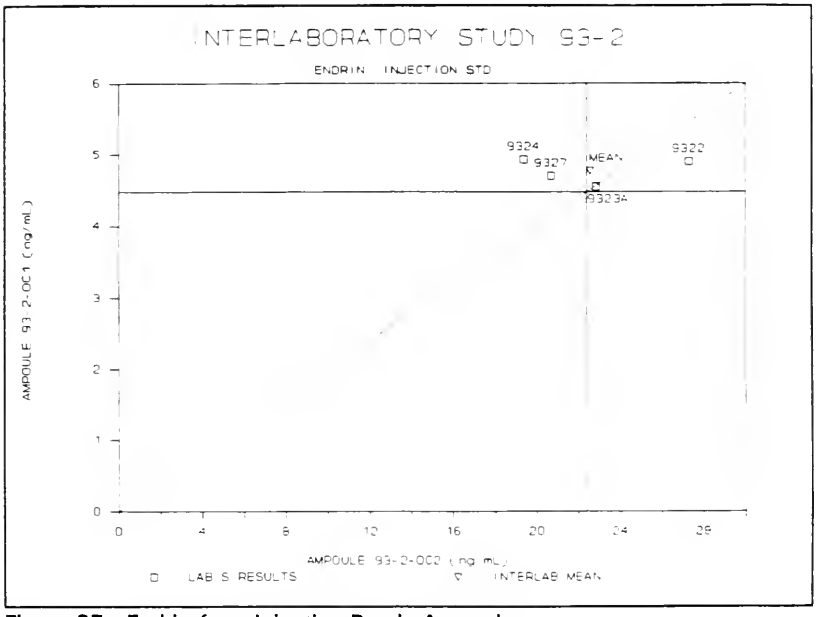

Figure 27 - Endrin from Injection-Ready Ampoules

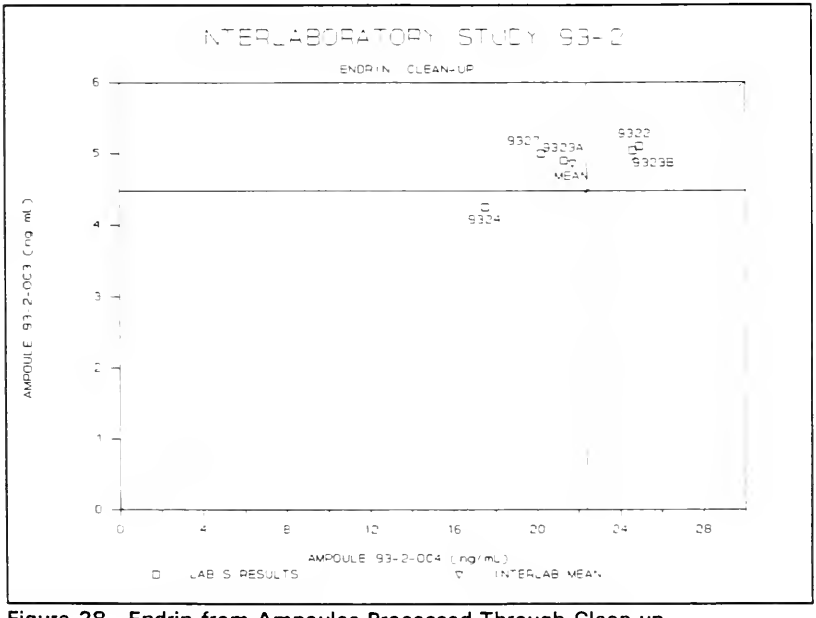

Figure 28 - Endrin from Ampoules Processed Through Clean-up

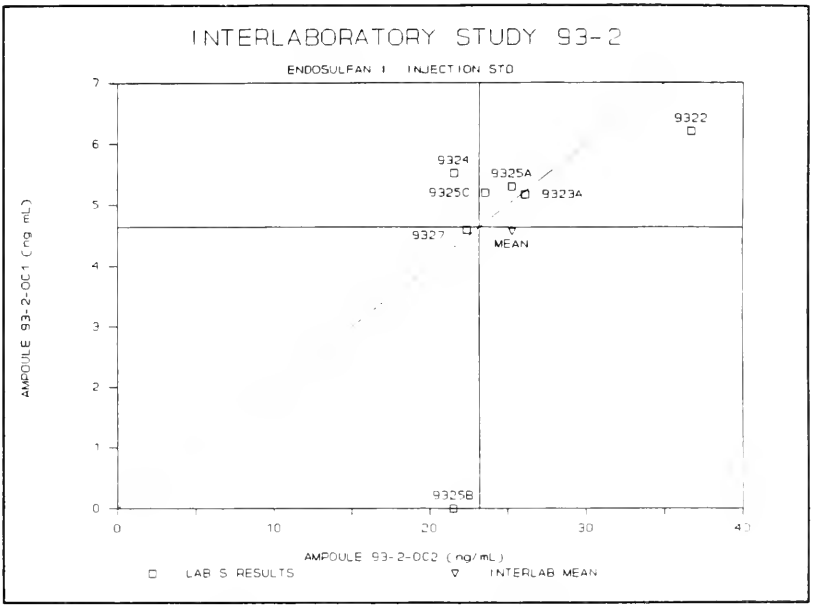

Figure 29 - Endosulfan I from Injection-Ready Ampoules

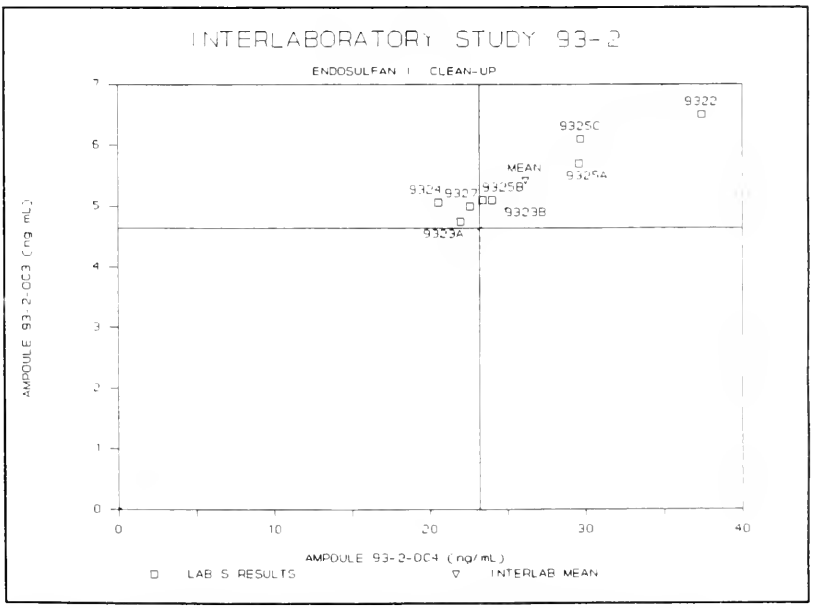

Figure 30 - Endosulfan I from Ampoules Processed Through Clean-up

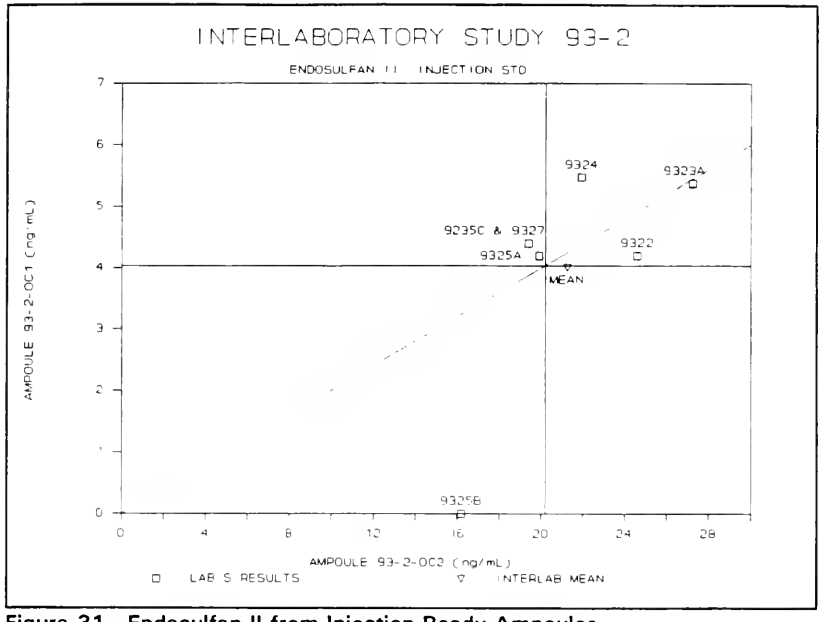

Figure 31 - Endosulfan II from Injection-Ready Ampoules

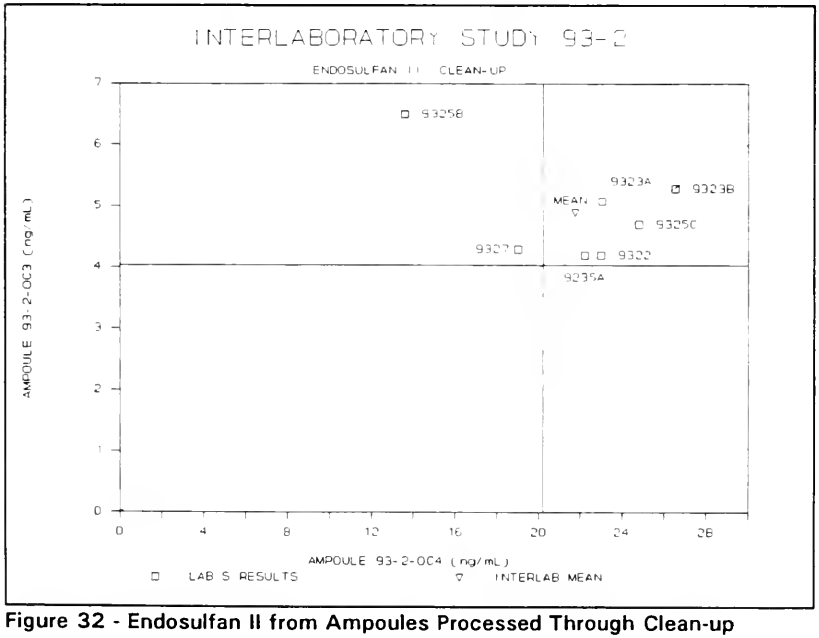

Figure 32 - Endosulfan II from Ampoules Processed Through Clean-up

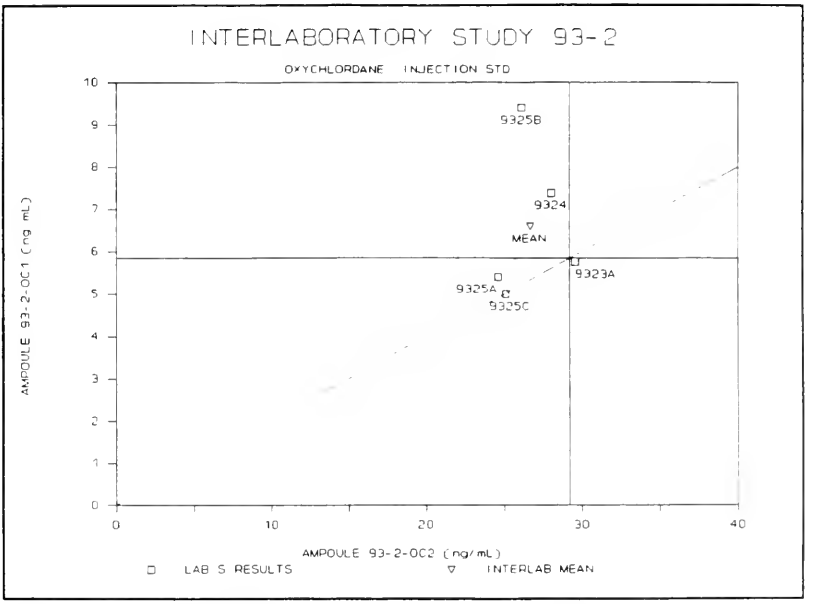

Figure 33 - Oxychlordane from Injection-Ready Ampoules

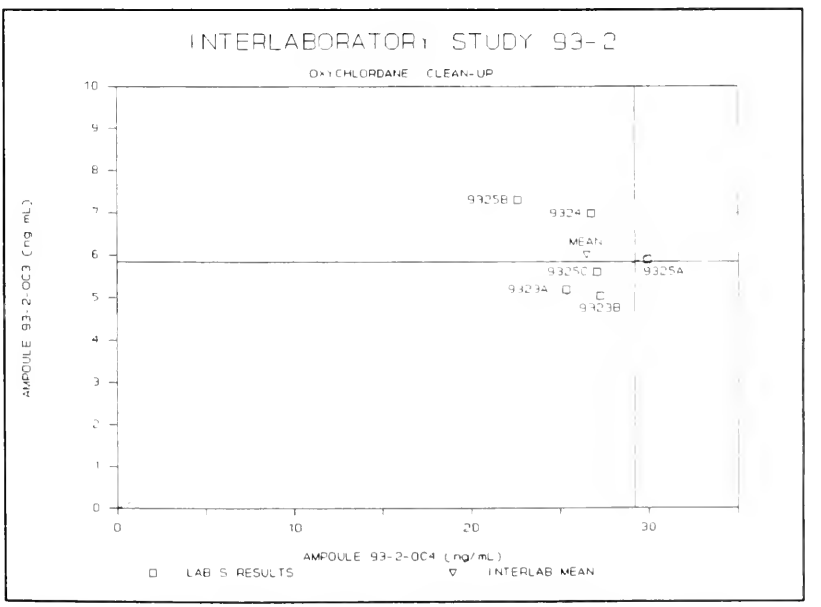

Figure 34 - Oxychlordane from Ampoules Processed Through Clean-up

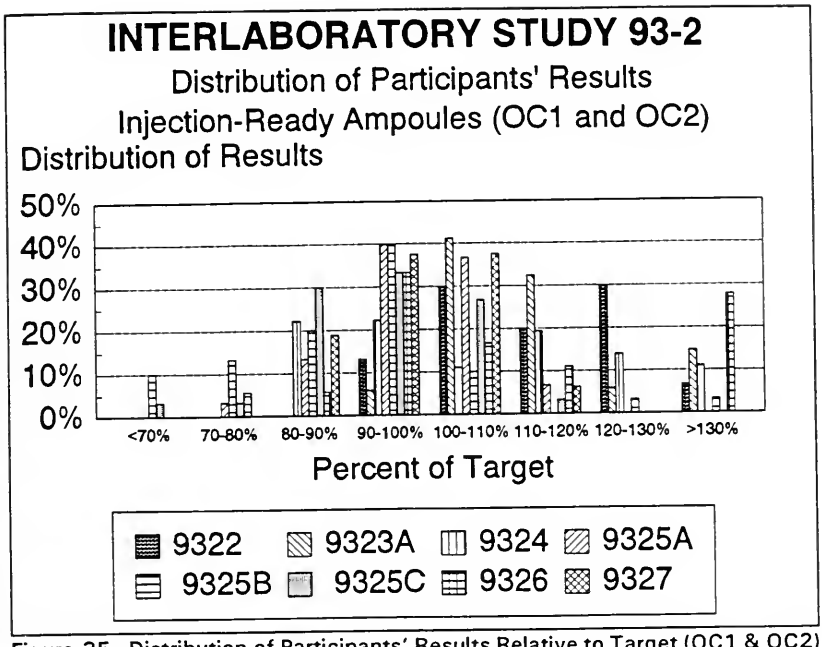

Figure 35 - Distribution of Participants' Results Relative to Target (OC1 & OC2)

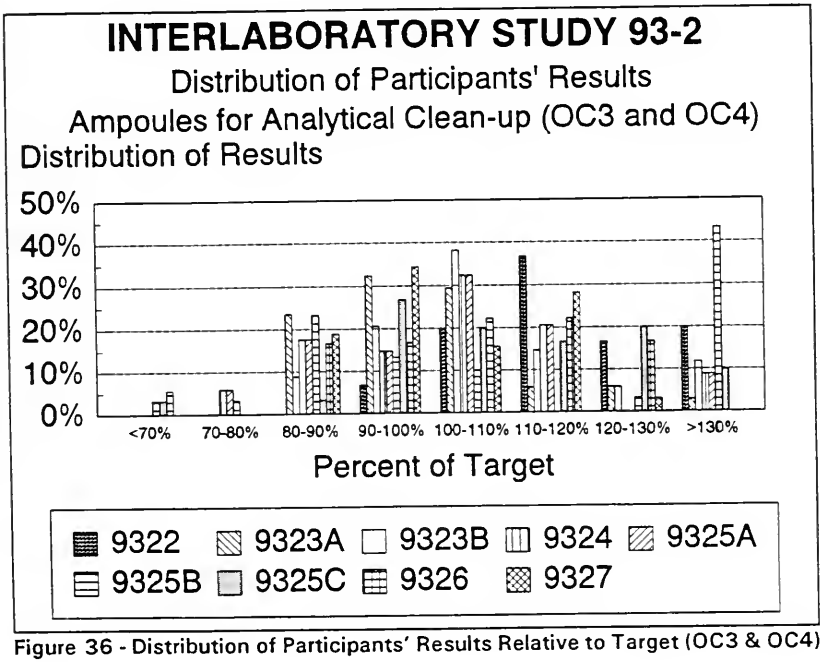

Figure 36 - Distribution of Participants' Results Relative to Target (OC3 & OC4)

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

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ARQP
4905 Dufferin St.
Downsview, Ontario
M3H 5T4
(416) 739-4847

July 27, 1993

Dear Interlaboratory Study 93-2 Participant,

Please find enclosed four 5 mL ampoules for the analysis of Organochlorine Pesticides. The ampoules are labelled 93-2-OC1, 93-2-OC2, 93-2-OC3, and 93-2-OC4 and all are in iso-octane. If you are missing any of the ampoules or they have broken in transit, please contact Sathi Selliah at (416) 235-5700 immediately for replacement. Please read the following instructions carefully. Please store all solutions below 0°C.

Ampoules 93-2-OC1 and 93-2-OC2

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form.

Ampoules 93-2-OC3 and 93-2-OC4

These solutions require analytical Clean-up prior to instrumental analysis. Please note that there is an interferant present that must be removed by the Clean-up process. Please provide all the indicated information on the accompanying report form.

Please report all results on the accompanying form by September 17, 1993.

Thank you for your participation in this study. Please contact me if you have any questions or problems.

Your identification code is:

Sylvia Cussion
Air Toxics Quality Assurance Officer
(416) 739-4847
FAX (416) 739-5708

INTERLABORATORY STUDY 93-2

ORGANOCHLORINE PESTICIDES (OC'S)
FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

	93-2-OC1		93-2-OC2	
PARAMETER	**Dil. Factor**	**Result**	**Dil. Factor**	**Result**
α-Hexachlorocyclohexane (α-HCH)				
γ-Hexachlorocyclohexane (γ-HCH)				
p,p-DDT				
o,p-DDT				
p,p-DDD				
o,p-DDD				
p,p-DDE				
o,p-DDE				
α-Chlordane				
γ-Chlordane				
Heptachlor Epoxide				
Methoxychlor				
Dieldrin				
Hexachlorobenzene (HCB)				
Endrin				
Endosulfan I				
Endosulfan II				
Oxychlordane				

Dil. Factor = Dilution Factor

INSTRUMENT AND DETECTOR USED FOR ANALYSIS:

GC COLUMN:

INTERLABORATORY STUDY 93-2

ORGANOCHLORINE PESTICIDES (OC'S)
FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

	93-2-OC3		93-2-OC4	
PARAMETER	Dil. Factor	Result	Dil. Factor	Result
α-Hexachlorocyclohexane (*α*-HCH)				
γ-Hexachlorocyclohexane (*γ*-HCH)				
p,p-DDT				
o,p-DDT				
p,p-DDD				
o,p-DDD				
p,p-DDE				
o,p-DDE				
α-Chlordane				
γ-Chlordane				
Heptachlor Epoxide				
Methoxychlor				
Dieldrin				
Hexachlorobenzene (HCB)				
Endrin				
Endosulfan I				
Endosulfan II				
Oxychlordane				

Dil. Factor = Dilution Factor

SAMPLE VOLUME USED FOR Clean-up:

SOLVENT(S) USED FOR CLEAN-UP:

COLUMN PACKING MATERIAL:

FINAL SAMPLE VOLUME:

ARQP
4905 Dufferin St.
Downsview, Ontario
M3H 5T4
(416) 739-4847

November 19, 1993

Dear Participant of Interlaboratory Study 93-2,

Please find enclosed the table of results from Interlaboratory Study 93-2 for the analysis of Organochlorine Pesticides (OC's). If there are any transcription errors, please contact me at (416) 739-4847 by December 3, 1993.

A final report will be provided to all participants.

Your identification code is:

Sincerely,

Sylvia Cussion
Air Toxics Quality Assurance Officer
(416) 739-4847

ARQP
4905 Dufferin St.
Downsview, Ontario
M3H 5T4
(416) 739-4847

December 8, 1993

Dear Participant of Interlaboratory Study 93-2,

The table of results from Interlaboratory Study 93-2 for the analysis of Organochlorine Pesticides (OC's) was distributed to all participants on November 19, 1993.

Laboratory 9323 noted a transcription error in their duplicate results for Ampoule 93-2-OC3, for 6 parameters. The results labelled "A" were also entered in the column "B". The correct "B" results have been entered and are highlighted in the table.

Laboratory 9325 had submitted results using GC/MS (labelled "B") and reported the results with 0 decimal places. In the interim between submitting their results and the release of the complete table of results, further development work established the reliability of reporting to 1 decimal place. They have resubmitted their original results reporting 1 decimal place. These values have been entered into the tables with their original values enclosed in brackets.

The statistical calculations were reworked to incorporate the above corrections and revisions. Please find enclosed a revised set of tables. These are the final values that will be incorporated into the formal report. This report will be provided to all participants.

Your identification code is:

Sincerely,

Sylvia Cussion
Air Toxics Quality Assurance Officer
(416) 739-4847